PB83-259671

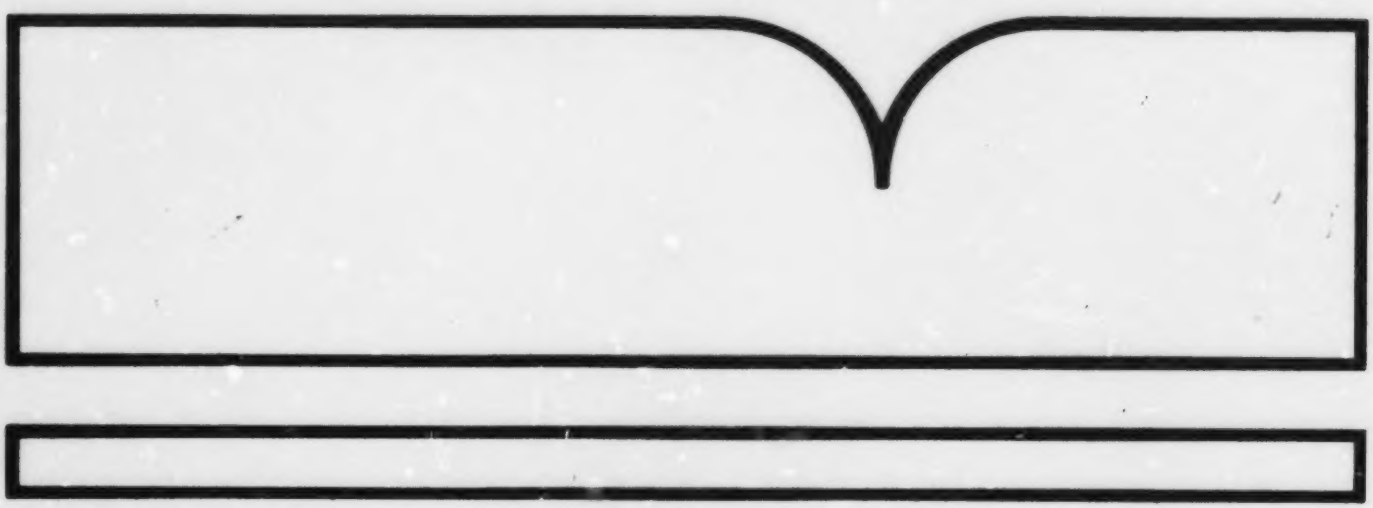
Cyanide Removal from Coke Making and Blast Furnace Waste Waters

Michigan Technological Univ., Houghton

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Aug 83



U.S. Department of Commerce
National Technical Information Service
NTIS

PB83-259671

EPA-600/2-83-066
August 1983

CYANIDE REMOVAL FROM COKE MAKING AND BLAST FURNACE WASTE WATERS

by

G. W. Lower, D. J. Spottiswood

Michigan Technological University
Houghton, Michigan 49931

Research Grant R805807010

Cooperative Agreement CR807818010 (EPA); 78-405 (AISI)

EPA Project Officer: Robert C. McCrillis

Industrial Environmental Research Laboratory
Industrial Processes Branch
Research Triangle Park, N.C. 27711

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

and

AMERICAN IRON AND STEEL INSTITUTE
1000 16th Street, N. W.
Washington, D. C. 20036

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-83-066	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE: Cyanide Removal from Coke Making and Blast Furnace Waste Waters	5. REPORT DATE: August 1983
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): G. W. Lower and D. J. Spottiswood**	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Michigan Technological University, Houghton, Michigan 49931	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.: R805807 and CR807818
12. SPONSORING AGENCY NAME AND ADDRESS: EPA, Office of Research and Development* Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED: Final; 8/78 - 3/82
	14. SPONSORING AGENCY CODE: EPA/600/13

15. SUPPLEMENTARY NOTES: IERL-RTP project officer is Robert C. McCrillis, Mail Drop 63, 919/541-2733. (*) Cosponsored by American Iron and Steel Institute. (**) Now with Colorado School of Mines, Golden, Colorado 80401.

16. ABSTRACT: The report gives results of a study to determine the feasibility of removing cyanide from coke making and blast furnace waste waters by ion flotation or column precipitate flotation of iron ferrocyanides. Ion flotation was reasonably effective on ferricyanide, but not on cyanide or ferrocyanide; therefore, efforts were concentrated on the formation and flotation of iron ferrocyanide precipitates. Note that a readily available source of ferrous iron is waste pickle liquors. Test results showed that 95-99% cyanide could be recovered from synthetic solutions containing 100 mg/liter cyanide, and 91% from intercepting sump waters (ISW). (Synthetic ferrocyanide solutions, free cyanide solutions, and two coke plant waste waters--crude ammonia liquor (CAL) and ISW--were tested.) The most effective flotation reagent was a primary amine (dodecylamine acetate), and the most important variable in the process was the pH of flotation. Test results also showed that precipitate flotation can be used as a primary process to remove most of the cyanide and could be used to meet effluent limitations under certain conditions, depending on feed concentration and volume. Ion exchange tests on synthetic solutions produced effluents which met discharge standards. This may be one possible secondary method of treatment; however, no work was done on flotation effluents or plant liquors.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Amines	Stationary Sources	07B, 07C
Cyanides	Iron Ferrocyanides	
Waste Water		13H
Coking		11F
Blast Furnaces		14G
Precipitates		

18. DISTRIBUTION STATEMENT: Release to Public	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 64
	20. SECURITY CLASS (This page): Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

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ABSTRACT

This research program was initiated with the objective of determining the feasibility of removing cyanide from coke making and blast furnace waste waters by column precipitate flotation of iron ferrocyanides. It should be noted that a readily available source of ferrous iron is obtainable from waste pickle liquor.

An experimental program was designed to evaluate the effect of operational variables (iron addition; reaction time to form the iron cyanide complex; conditioning time; flotation time; and air flow rates). Synthetic ferrocyanide solutions, free cyanide solutions, and two coke plant waste waters [crude ammonia liquor (CAL) and intercepting sump water (ISW)] were tested. Batch and continuous column flotation tests were run. Wet oxidation tests were conducted on the froth product.

Results of the tests showed that cyanide recoveries of 95-99% could be obtained from the synthetic solutions containing 100 mg/ℓ cyanide and recoveries of 91% from intercepting sump waters. The most effective flotation reagent was a primary amine, dodecylamine acetate, and the most important variable in the process was the pH of flotation. A set of operating conditions (iron addition, collector addition, pH, reaction time, conditioning time, and flotation time) were developed for both the synthetic solutions and a coke plant waste water (ISW). Preliminary wet oxidation tests indicated that the froth product could be converted to ammonia and ferric oxide by wet oxidation.

Results showed that the precipitate flotation process definitely could be used as a primary process for cyanide removal and under certain conditions (low total effluent volume) could produce an acceptable final effluent.

Ion flotation, using a quaternary amine was reasonably effective on ferricyanide but less effective on cyanide and ferrocyanide.

Ion exchange tests on synthetic solutions produced effluents which met discharge standards. This may be one possible secondary method of treatment. However, no work was done on flotation effluents or plant liquors.

It was also noted in this test program that the iron-iron cyanide precipitate settled quite rapidly once it was formed. Although no work was done in this area, it is possible that the bulk of the cyanide could be removed by precipitation and thickening, followed by wet oxidation of the thickener underflow.

This report was submitted by Michigan Technological University in fulfillment of work co-sponsored by the U.S. Environmental Protection Agency (Grant R805807010 and Cooperative Agreement CR807818010) and the American Iron and Steel Institute (Project No. 78-405). The project was initiated August 1, 1978 and completed March 23, 1982.

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SECTION 1

INTRODUCTION

Fifty years ago coke production from by-product ovens surpassed coke production from beehive ovens (1). The advantages of by-product processing were that it reduced the air pollution problems associated with coking, and recovered marketable by-product chemicals. However, the gas processing introduced a significant water pollution problem. The problem was formally defined by the United States Environmental Protection Agency (EPA) following the passage of the Federal Water Pollution Control Act Amendment in 1972 (P.L. 92-500).

In May, 1982 the EPA issued final regulations defining iron and steel manufacturing point source category effluent limitations guidelines (2). For by-product coke making, these regulations set a thirty-day average limitation of 0.00351 kilograms of cyanide per metric ton of coke by application of the best available technology economically achievable (BAT).

In addition to the cyanide, the plant liquors contain fixed and free ammonia, free and emulsified oils, phenols, and various suspended solids. These contaminants are the by-product of the pyrolysis reactions occurring during the carbonization of coal. The contamination of the process waters occurs during the processing of the coke oven gas for the recovery of coal chemicals. The plant contains three major process streams: (1) the crude ammonia liquors, (2) the barometric condenser liquors, and (3) the intercepting sump water (3). The crude ammonia liquors (also referred to as waste ammonia liquors) are the condensed water vapors separated from tar in the tar plant. The barometric condenser liquors result from the direct contact of cooling water with vapors released in the crystallizing and concentrating of ammonium sulfate by vacuum evaporation. The intercepting sump water is a combination of the water from the oil-water separators and the various drains throughout the plant. Typical contaminant loading and flow rates of these streams are shown in Table 1 for a plant producing 5442 metric tons (6000 short tons) of coke per day (3).

Cyanide concentration limits in the combined effluent will vary from plant to plant depending on the total effluent volume. For the above plant the total effluent volume would be 1452 liters per metric ton of coke produced. The cyanide concentration in the combined effluent would be 50.3 g/ℓ. Based on BAT limitations, this would require reducing the effluent cyanide concentration to no more than 2.42 mg/ℓ.

In a second plant process improvements greatly reduced the total effluent volume primarily by improvements in the ammonium sulfate condenser system (Private Communication). In this plant producing 2721 metric tons (3000 short tons) of coke per day the total effluent volume is 681 liters

TABLE 1. COKE PLANT WASTE WATER STREAMS (5442 TPD COKE)

Stream	Flow m^3/min	Ammonia mg/ℓ	Phenol mg/ℓ	Cyanide mg/ℓ	Oil mg/ℓ
Crude Ammonia Liquor	0.57	5000	2000	20	1000
Barometric Condenser Water	3.80	20	40	40	20
Intercepting Sump Water	1.14	150	300	100	10,000

per metric ton of coke. The combined effluent would analyze 56.8 mg/ℓ CN and the BAT effluent cyanide limitation would be 5.16 mg/ℓ.

There are two general approaches toward detoxifying cyanide wastes. The first is to oxidize the cyanide while it is in the process stream. The second is to remove the cyanide from the main stream and then oxidize the cyanide concentrate. The advantage to treating the entire stream with an oxidant is the elimination of the separation step. A major economic factor is the chemical oxygen demand (C.O.D.) of the system. The greater the C.O.D. the more oxidant required, which increases costs.

Chlorine has been commonly used in the oxidation of cyanides in electroplating wastes (4). However, there are limitations on residual chlorine in effluents and in coke making waste water and there is the possibility of producing chlorinated organics such as PCB. Oxidation with ozone does not pose these problems and the cost of ozonation compares favorably to chlorination (5). Unfortunately, the ozonation of iron cyanide complexes requires ultraviolet light to first decompose the otherwise refractory complex (6).

Dupont has registered a process with the trade name Kastone which can oxidize free cyanide with hydrogen peroxide (7). It is not known if the process is applicable to coke plant waste water. An electroflotation process has also been used to oxidize cyanide wastes with subsequent recovery of the heavy metal (8). This process is more adapted to plating wastes. Activated sludge systems have been used to treat coke plant waste (9). Results indicate that fluctuations in temperature and excessive levels of toxic chemicals like cyanide and ammonia will have a detrimental effect on the biological activity and require long acclimation times (10).

Various methods have been investigated to concentrate cyanide wastes, both in coke plants and other sources. Iron cyanide complexes have been removed on a pilot plant scale from aluminum reduction plant waste waters using an ion exchange process (11). Grieves and Bhattacharyya (12) reported that precipitated iron cyanide can be floated from aqueous suspensions with a cationic surfactant. They reported an optimum 95 percent recovery of complexed cyanide at a pH of 6. About 7 mg/ℓ of free cyanide remained in solution. Clarke and Wilson (13) reported that adsorbing colloid flotation (A.C.F.) removed 92 percent of the free cyanide at an optimum pH of 5.5.

With A.C.F., the iron cyanide precipitate was adsorbed onto $Fe(OH)_3$ floc. The surfactant was sodium lauryl sulfate. Bucsh and Lower (14) showed that complexed ferricyanide could be concentrated using an ion flotation technique.

Szarawara (15) has shown that upon addition of ferrous iron to cyanide solutions, the cyanide concentration would be at a minimum between pH 8 and 9 as a result of the formation of the complex $Fe(CN)_6^{-4}$ followed by precipitation of $Fe_2Fe(CN)_6$. In review of his work it should be noted that Szarawara made no reference to the oxidation of ferrous iron. The potential of the Fe^{+3}/Fe^{+2} couple is such that molecular oxygen can oxidize ferrous to ferric iron in aqueous solutions (16). Stumm and Lee (17) reported that the oxidation kinetics become very favorable above pH 6. Prober (18) reported that ferricyanide complex formation in simulated coke plant effluents is very slow compared to ferrocyanide formation. He states that both complex formation rates are greater in the pH range of pH 7.5 to pH 10.5. It should be noted that $Fe(OH)_3$ has a low solubility product (19). Thus the oxidation of iron and the formation of $Fe(OH)_3$ will reduce the amount of iron available for complexing.

The primary objective of this study was to develop a process for the removal of cyanide from coke making waters by precipitate flotation of iron ferrocyanides. This process involves addition of ferrous iron to form a ferrocyanide complex from free cyanide, precipitation of ferrous ferrocyanide, and subsequent flotation of the iron cyanide precipitate. It should be noted that pickle liquor is a readily available source of ferrous iron.

Secondary studies involved cyanide removal by ion exchange adsorption of ferrocyanide and by ion flotation ferricyanide. The studies were conducted simultaneously at Michigan Technological University by Dr. George W. Lower and at the Colorado School of Mines by Dr. D. J. Spottiswood. The precipitate flotation work at Michigan Technological University was directed toward establishing the optimum formation of the iron ferrocyanides, selection of flotation reagents, and batch column flotation from both synthetic and plant liquors. In addition, limited work was done on disposal of the flotation concentrate and on ion exchange. This work is presented in Section 5. The work at Colorado School of Mines was directed toward continuous column precipitate flotation and is presented in Section 6. Ion flotation studies were carried out at Michigan Technological University and the results are given in Section 7.

SECTION 2

CONCLUSIONS

The results of experimental studies on the removal of cyanide from coke making and simulated blast furnace waste waters by amine flotation of iron ferrocyanide precipitates have indicated that the bulk of the cyanide could be removed by this method. Final effluent standards were achieved for coke making waste waters when the total volume of effluent per ton of coke was reduced.

Cyanide recoveries of 95-99% were obtained from both ferrocyanide solutions and non-complexed cyanide solutions containing 100 mg/ℓ cyanide plus high salt concentrations. Cyanide recoveries of as high as 91% were obtained from a coke plant liquor (intercepting sump water) containing 89 mg/ℓ cyanide.

The most important variable in the process was pH and the most efficient collector was a primary amine, dodecylamine acetate at pH 8. A quaternary amine, aliquat A-336, was effective up to pH 6 but recoveries dropped sharply at higher pH values.

Ion exchange using a strong base resin was capable of producing an acceptable effluent (less than 0.25 mg/ℓ cyanide) from synthetic solutions containing 25 mg/ℓ cyanide as ferrocyanide plus 5000 mg/ℓ chloride. However, the effectiveness of this process as a secondary stage following flotation was not determined.

Preliminary tests indicated that the cyanide in the froth flotation product could be effectively destroyed by wet oxidation. The solid oxidation product (iron oxide) met the EP Toxicity standards.

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SECTION 3

RECOMMENDATIONS

The bulk removal of cyanide from coke making and blast furnace waste waters by formation and flotation of iron ferrocyanide precipitates should continue to be investigated. This should be done on a continuous basis preferably at a steel mill site. Both column and submerged air flotation should be studied. In addition, the possibility of precipitation and solid-liquid separation by thickening should be considered.

Further studies on destruction of the cyanide precipitate by wet oxidation should be made in order to determine the optimum operating conditions and the recoveries of the process.

Ion exchange studies should be carried out on the flotation or thickener effluent if an acceptable recycle process cannot be carried out in order to determine if an acceptable discharge effluent can be produced.

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SECTION 4

EXPERIMENTAL PROCEDURES

FLOTATION

All flotation tests were batch tests carried out in a column fitted with a sintered glass diffuser at the bottom of the column as shown in Figure 1. The solutions to be treated were conditioned for a given period of time in a conditioning cell equipped with a stirrer. The resulting slurry was then poured into the flotation column, air introduced into the column and the slurry floated for a given period of time. The froth product was removed at the top of the column by an overflow launder.

Tests were conducted on synthetic solutions of both $K_4Fe(CN)_6$ and KCN prepared in tap water. All synthetic solutions tested contained 100 mg/ℓ total cyanide. Some synthetic solutions also contained 5000 mg/ℓ NaCl. Tests were also conducted on coke plant effluents obtained from the Republic Steel Plant in Cleveland, Ohio.

All tests involved adding $FeSO_4 \cdot 7\ H_2O$ to one liter of solution in the conditioning cell followed by addition of a surfactant (collector). Two or three reactions are involved during the conditioning period depending on whether the cyanide present is free or complexed. If the cyanide is free the reactions involved are complexing, precipitation, and adsorption reactions. Consequently, two conditioning times were considered, one for the complexing and precipitation reaction (called reaction time) and the other for collector adsorption (termed the adsorption time).

The air flow rate was kept at 400 cm^3 per minute. This is equivalent to 23.1 cm^3 per minute per square centimeter of bed or 0.4 volumes of air per minute per unit volume of solution. The froth was allowed to overflow the entire perimeter of the column top into a circular launder. The froth was then funneled into a graduated cylinder. The collapsed froth volumes were measured to determine the water split. A sample port at the bottom of the column permitted sampling the underflow. The column underflow was analyzed for total cyanide.

Several flotation reagents were tested. Their structures are listed in Table 2. The low solubility of Aliquat 366 required that it first be dissolved in isopropanol in order for it to disperse when added to the solution. Otherwise, the reagent when added to the water would tend to coagulate into little waxy balls. All chemicals used in the experiment were reagent grade. The $FeSO_4 \cdot 7\ H_2O$ was pre-dissolved in acidified tap water. The KCN and

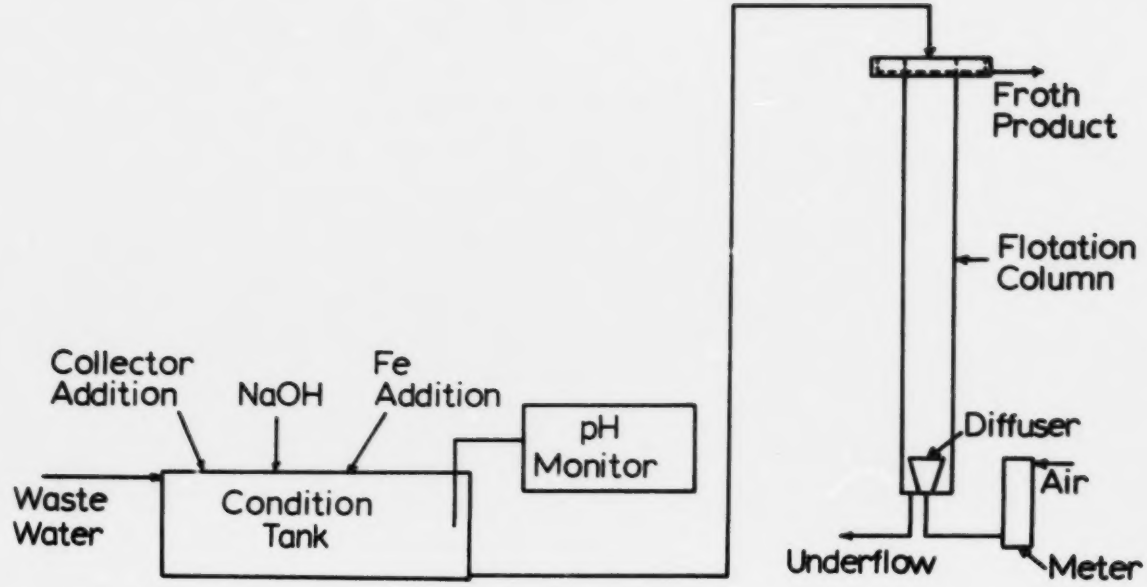

Fig. 1. Flotation column.

TABLE 2. FLOTATION REAGENTS

Reagent Name	Manufacturer	M.W.	Formula
ARMAC® 12D Dodecylamine Distilled acetate	Armour Industrial Chemical Company	245	$CH_3(CH_3)_{11}NH_3OCOCH_3$
Sodium Lauryl Sulfate	Aldrich Chemical Company	288	$CH_3(CH_2)_{11}OSO_3Na$
Aliquat 336 Tricaprylyl Methyl Ammonium Chloride	General Mills Chemical Division	x = 442	R_3NCH_3Cl R = C_8 - C_{10} carbon
4-Methyl 2-Pentanol (MIBC)	Unknown	102	$(CH_3)_2CHCH_2CHOHCH_3$

$K_4Fe(CN)_6$ were pre-dissolved in slightly alkaline tap water. It was important that fresh solutions be prepared daily to obtain consistent results. Details of the equipment are listed in Table 3.

TABLE 3. EQUIPMENT DESCRIPTION

Equipment Name	Manufacturer - Model	Dimensions	Material
Foam Separation Column & Bubbler	Fabricated	Cylindrical Height 70 cm ID 4.7 cm Bubbler OD 4.4 cm	Pyrex® Sintered Glass Frit 10-15 u
Conditioning Cell	Unknown	Cylindrical 3000 ml beaker	Pyrex®
Lab Stirrer	T - Line	Model #704 Variable Speed	
Impeller	Fabricated	4 Blade Diameter = 55mm Blade Width 8mm Blade Thickness 3mm Square Pitch	Steel
pH Meter	Radiometer Copenhagen	Model #PHN162	
Rotameter	Matheson Co.	Tube Size 603	
Timer	Eastman Kodak Co.	Kodak Timer	
Tachometer	GEN-A-TAK	Model #6	

ION EXCHANGE

Ion exchange tests were carried out using a 40 cm diameter column containing 200 mℓ of backwashed wet settled resin. The resin bed depth was 16.0 cm. The resin used was IRA-958 (Rohm and Haas Co.), a strong base resin. Feed solutions contained 25 mg/ℓ cyanide (as ferrocyanide) plus 5000 ppm chloride at pH 7.5 to 8.0. The column effluent was analyzed for cyanide as were the composite barren solutions. The breakthrough point was selected to be 0.25 ppm cyanide. Effluent volumes are reported in bed volumes (BV) wherein one bed volume is equal to 0.20 liters. That is the number of bed volumes of solution passed through the resin is equivalent to the volume of solution per volume of resin bed. In all tests except Tests 6 and 7, the elution was carried out using 15% NaCl solution containing 1.4 g/ℓ NaOH. The pH of these solutions was 12.2 but pH readings in high chloride solutions are somewhat suspect. In Test 6 the pH was 9.0 and in Test 7 it was 10.2.

ANALYTICAL PROCEDURE

Cyanide assays were performed by the ASTM standard method for cyanides in water (20). In this method, total cyanide after distillation is determined. The distillate is assayed by the silver nitrate titration method for high cyanide concentrations and by the pyridine-barbaturic acid colorimetric method for low cyanide concentrations. The cuprous chloride catalyst was replaced by 10.0 mℓ of saturated $HgCl_2$ and 40.0 mℓ of 2.5 M $MgCl_2$ per distillation. The reagents used for the colorimetric assays were those of Lambert et al (21).

SECTION 5

RESULTS AND DISCUSSION

FLOTATION

The effectiveness of each flotation test was determined by calculating the fraction removed (Fr) and the removal factor (RF). The fraction removed and the removal factor are defined by the following equations:

$$Fr = \frac{A_f V_f - A_u V_u}{A_f V_f}$$

$$RF = 1 - \frac{Au}{A_f}$$

The symbols A_f and Au represent the cyanide assays of the feed and the underflow respectively. The volumes of the feed and the underflow are represented by V_f and V_u. The fraction removed is simply the fraction of the total cyanide units that report to the overflow and is dependent on the water split between the overflow and the underflow. The removal factor is equivalent to the fraction removed when the overflow volume is zero and is independent of the water split. For any test the difference between Fr and RF indicates the portion of the total recovery due to the water split.

The results will be discussed in two parts, first using synthetic liquors and secondly, using coke plant liquors. The synthetic solutions will function as the model system and serve as a basis for interpreting the results obtained when using the coke plant liquors.

Synthetic Ferrocyanide Solutions

The first major set of experiments were done using Aliquat 336(A336) as the surfactant. Aliquat 336 is a quaternary amine developed by General Mills Chemical Division. Bucsh (14), using an ion flotation technique stated that A336 was effective in removing ferricyanide ions. It was therefore anticipated that if A336 would activate iron cyanide precipitates, the additional recovery of any ferricyanide ions in solution would give higher recoveries of the total cyanide in solution.

Major Variables--

A factorial experiment was designed to study the effects of the following variables: iron addition, surfactant addition, and pH. The conditioning time was held constant at 15 minutes and the flotation time at 5 minutes. The two levels of total Fe II represent a 7 molar and a 70 molar percent

excess iron over total cyanide. The excess is based upon the formation of Prussian Blue ($Fe_4(Fe(CN)_6)_3$. The cyanide was added as $K_4Fe(CN)_6$. The iron in the $K_4Fe(CN)_6$ is included in the above figures. The additional iron was added as $FeSO_4 \cdot 7\ H_2O$ as described in the experimental section. The pH was adjusted and the surfactant was added immediately thereafter. Thus for the initial experiments using $K_4Fe(CN)_6$ the stated conditioning times included simultaneous precipitation and surfactant adsorption time. The complexed cyanide was used to promote rapid precipitate formation. The results shown in Table 4 indicate that the pH has the greatest effect on recovery. Precipitation reactions occurred immediately after the $FeSO_4$ was added. At pH 3 the finely divided precipitates were a deep blue color which indicated Prussian Blue was forming. At pH 7 floc-like green precipitates formed. The green color probably resulted from a combination of Prussian Blue and $Fe(OH)_3$ precipitates. The additional precipitates probably consumed more of the surfactant and therefore less collector was available to act as a frother and as a collector for the precipitated cyanide. It should be noted, however, that increasing the amount of A336 did not improve recovery whereas higher levels of iron resulted in considerably higher recoveries.

TABLE 4. PRECIPITATION AND FLOTATION OF FERROCYANIDE

Test No.	Fe mg/ℓ (mM)	A336 mg/ℓ (mM)	pH	Fr	RF
1	90(1.6)	283(0.64)	3.0	0.54	.480
2	144(2.6)	283(0.64)	3.0	0.94	.910
3	90(1.6)	567(1.28)	3.0	0.66	.600
4	144(2.6)	567(1.28)	3.0	0.95	.915
5	90(1.6)	283(0.64)	7.0	0.10	.10
6	144(2.6)	283(0.64)	7.0	0.54	.54
7	90(1.6)	567(1.28)	7.0	.18	.18
8	144(2.6)	567(1.28)	7.0	.43	.42

A_f = 100 mg/ℓ Total CN (added as $K_4Fe(CN)_6$)

Effect of pH--

Based on the results of the above tests the effect of pH was investigated with the iron and the A336 levels held constant at 144 mg/ℓ and 283 mg/ℓ respectively. Figure 2 illustrates that recovery dramatically decreases above pH 6. Grieves and Bhattacharyya (12) reported similar results using the cationic surfactant ethyl hexadecyldimethylammonium bromide. They postulated that the decrease in recovery was caused by the precipitation of the excess ferrous ion. It should be noted however, that when they added additional surfactant the recovery did not improve significantly.

Collector Addition--

The effect of collector addition at pH 4 with 144 mg/ℓ total Fe II and a 5 minute conditioning time on cyanide recovery from tap water solution is

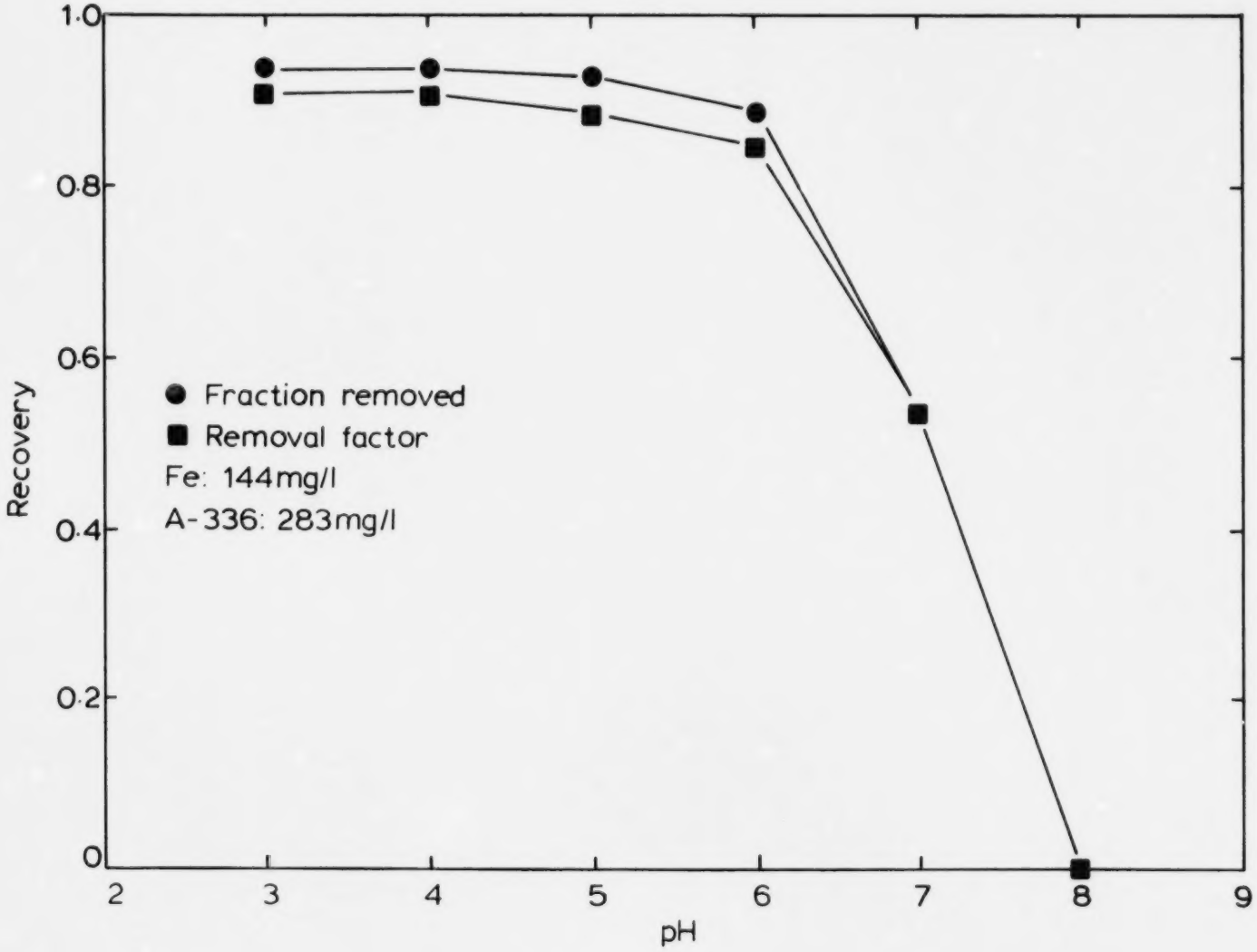

Fig. 2. The effect of pH on cyanide recovery from ferrocyanide solutions using collector A-336.

shown in Figure 3. The results of flotation from solutions containing 5000 mg/ℓ NaCl under the above conditions was also studied since coke waste waters contain high chloride concentrations. These results are shown in Figure 4. It should be noted that the five minute conditioning time provided recoveries similar to the fifteen minute conditioning times used earlier as shown in Figure 2. The results indicate that in tap water the recovery passes through a maximum at about 140 mg/ℓ of A336. This is in contrast to the behavior of chloride containing waters where cyanide recovery does not pass through a maximum but shows a steady increase with increasing collector addition. Higher recoveries were obtained from the water solutions at collector levels below 600 mg/ℓ. The effect of adding NaCl may reduce the activity of the surfactant and consequently more surfactant would be required to reach maximum recovery. The presence of NaCl could depress the system in several ways. The sodium cation could compete with the collector ions within the double layer, thereby reducing collector adsorption. The chloride anion could associate with the surfactant and reduce the sphere of influence of the surfactant's positive charge. The effect of increasing the ionic strength will also reduce the thickness of the diffuse part of the electrical double layer of the precipitates.

Synthetic Free Cyanide Solutions

In the following sequence of factorial tests KCN was used as the cyanide source. In this case a complexing reaction must take place prior to precipitation and flotation. The reaction time after addition of ferrous sulfate was 5 or 10 minutes. The collector was then added and the slurry conditioned for 5 minutes prior to flotation. The flotation time was held constant at 5 minutes. Two levels of iron addition were used. The effect of the presence of chloride was also studied. The collector concentration (A336) was 283 mg/ℓ and a constant pH of 4 was used.

As shown in Table 5 recoveries improved with increased reaction times in both water and chloride solutions. However, the greatest improvement was obtained by increasing the iron addition. In fact, at the higher iron level there was very little effect of reaction time on recovery. The increased iron concentration would be expected to shift both the complexing and precipitation reactions toward formation of the iron cyanide precipitate and thus improve recovery.

Collector Charge--

A factorial experiment was run to study the effect of collector charge on flotation from KCN solutions containing 5000 mg/ℓ NaCl. An anionic collector, sodium lauryl sulfate (NLS) and a cationic collector, dodecylamine acetate (12-D) were used at two collector levels and two pH levels. Both collectors have a twelve carbon chain. The iron addition was 215 mg/ℓ (165 mole excess of iron based on total cyanide). Reaction time, conditioning time, and flotation time, were each 5 minutes. As shown in Table 6, much higher recoveries were obtained with the amine collector than with the sulfate collector at pH 4. At pH 6 recoveries were considerably improved using the sulfate collector and somewhat improved with the amine collector. The best recovery was obtained using the amine collector at pH 6.

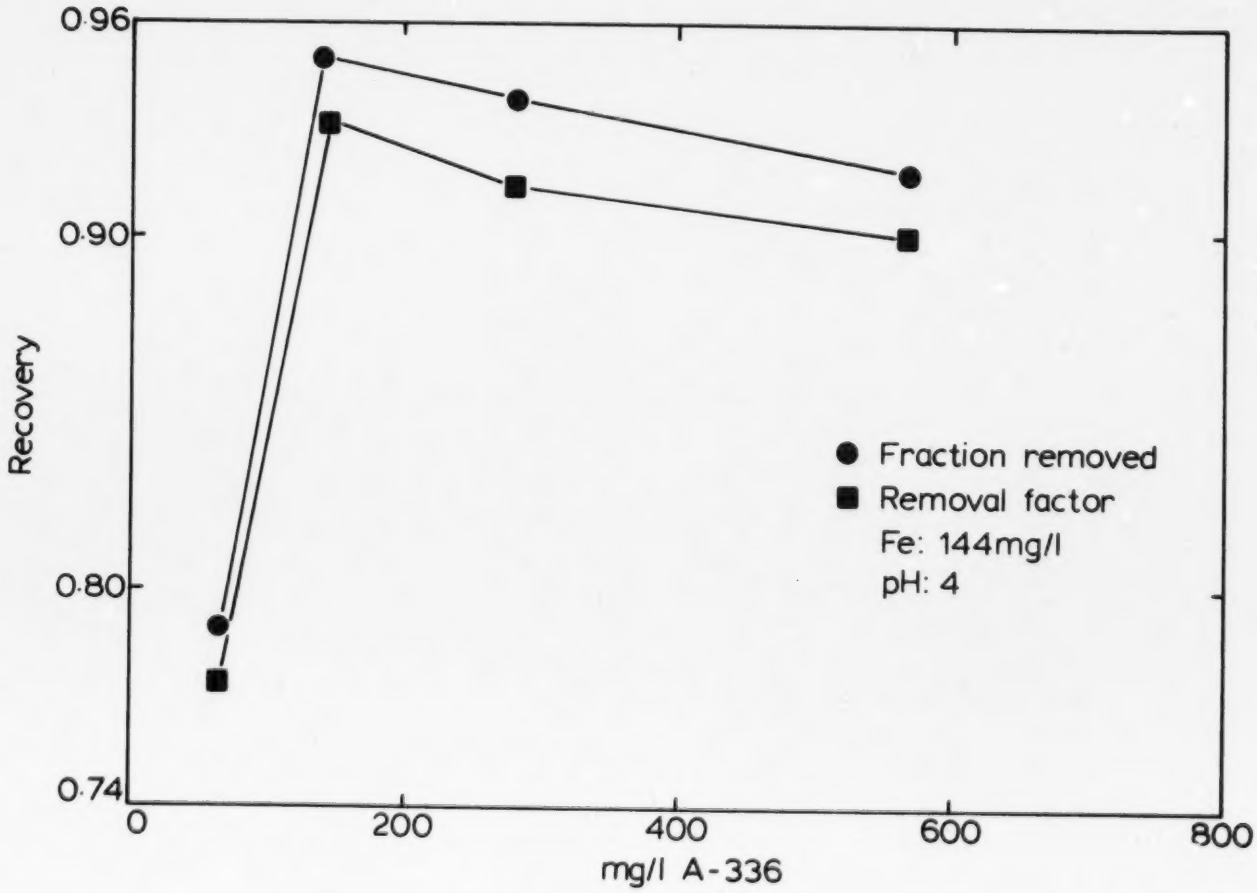

Fig. 3. The effect of collector dosage on cyanide recovery from ferrocyanide solutions.

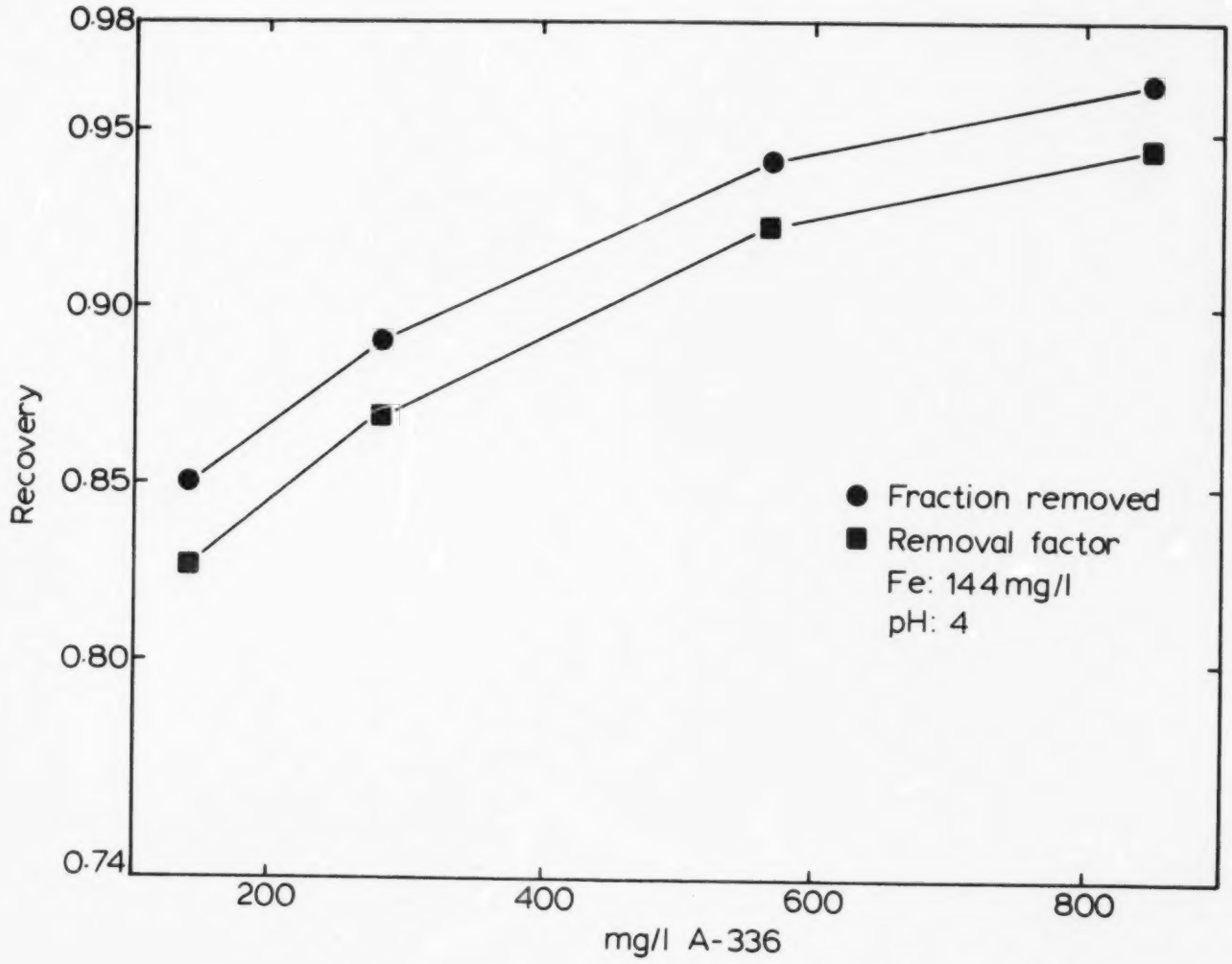

Fig. 4. The effect of collector dosage on cyanide recovery from ferrocyanide solutions containing 5000 mg/ℓ NaCl.

TABLE 5. FLOTATION FROM KCN SOLUTIONS WITH A336

Run	Ionic Strength	Reaction Time (min)	Fe II mg/ℓ	Fr	Rf
21	Tap Water	5.0	144	.69	.60
22	5000 mg/ℓ NaCl	5.0	144	.59	.56
23	Tap Water	10.0	144	.83	.78
24	5000 mg/ℓ NaCl	10.0	144	.71	.69
25	Tap Water	5.0	215	.91	.87
26	5000 mg/ℓ NaCl	5.0	215	.81	.78
27	Tap Water	10.0	215	.87	.77
28	5000 mg/ℓ NaCl	10.0	215	.78	.75

A = 100 mg/ℓ Total CN
pH = 4
A336 = 283 mg/ℓ

TABLE 6. EFFECT OF TYPE OF COLLECTOR

Run	Surfactant	Level mg/ℓ (mM)	pH	Fr	Rf
29	NLS	46.2(0.16)	4	.45	.28
30	12D	156(0.64)	4	.90	.88
31	NLS	23.1(0.08)	4	.42	.28
32	12D	31.3(0.13)	4	.87	.85
33	NLS	46.2(0.16)	6	.91	.89
34	12D	156(0.64)	6	.94	.80
36	NLS	23.1(0.08)	6	.84	.80
37	12D	31.3(0.13)	6	.90	.89

100 mg/ℓ Total CN
215 mg/ℓ Total Fe II

Effect of pH--

The effect of pH on recovery at a constant level of 46 mg/ℓ NLS was determined under the same conditions used in Table 6. As shown in Figure 5 there is a well defined maximum in recovery at pH 6. The oxidation of ferrous to ferric ion is much more rapid at the higher pH values. This leads to the formation of $Fe(OH)_3$ as the pH is raised. The zero point of charge of $Fe(OH)_3$ is somewhere in the range of pH 7 (22). Below pH 7 the $Fe(OH)_3$ particles have a positive charge and these should adsorb a negatively charged collector. In addition, previous work has indicated that the iron cyanide precipitate is

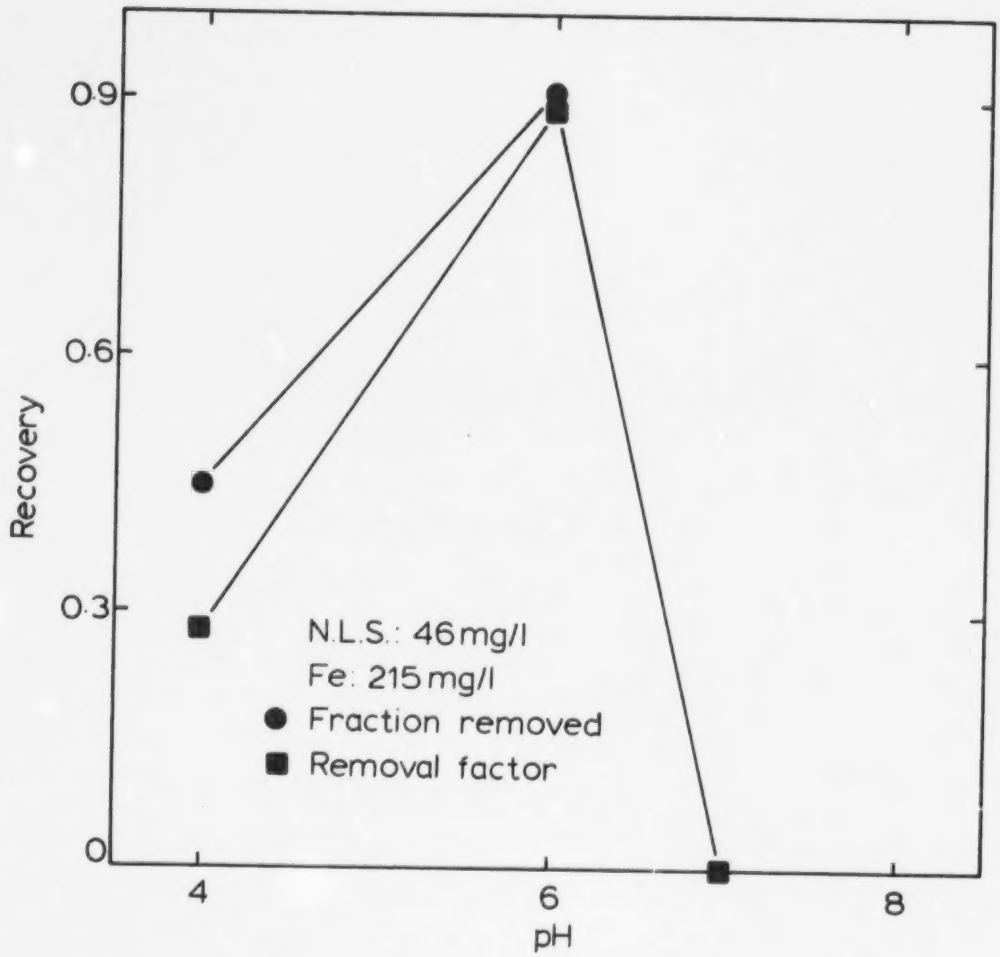

Fig. 5. The effect of pH on cyanide recovery from KCN-NaCl solutions using collector N.L.S.

negatively charged. It is postulated that the negatively charged iron cyanide precipitate adsorbs onto the positively charged iron hydroxide particles and the positively charged particles are floated with the negatively charged collector. Wilson and Clarke (13) describe this process as adsorbed colloid flotation. The recovery decreases below pH 6 because less $Fe(OH)_3$ is formed due to the slower rate of iron oxidation. Above pH 6 both particles and collectors are negatively charged, collector adsorption does not occur, and recovery drops to almost zero. It should be noted that above pH 6 the iron cyanide precipitates were not concentrated in the froth even though there was considerable froth. This indicates that entrainment of the precipitates in the rising foam is not the mechanism by which separation occurs. The particles must be surface active before the flotation column will concentrate them in the froth.

Flotation results using the positively charged collector 12-D at a level of 31 mg/ℓ as a function of pH under conditions similar to Figure 5 are shown in Figure 6. Recoveries obtained were equal to or better than those with the negatively charged NLS and much higher above pH 6. This increase in recovery with the amine above pH 7 occurs because both the ferric hydroxide and the iron cyanide precipitates are negatively charged. Maximum recovery was obtained at pH 8. Solution thermodynamics predicts the lowest equilibrium free cyanide level around pH 8 with excess ferrous ion. Thus, the driving force for the formation of ferrous cyanide precipitates is the greatest around pH 8. It is reasonable to assume that more iron cyanide precipitate will form where the driving force is greatest. A problem arises, however, due to the oxidation of the ferrous ion to ferric ion. The ferric ion is a much poorer complexing ion for cyanide than the ferrous ion (18). The excess ferrous iron serves to increase the driving force for complex formation. When this excess is reduced because of oxidation, less complex formation will occur. This would lead to lower cyanide recoveries. These results indicate that a 160 molar percent excess iron is sufficient to precipitate Prussian Blue from 100 mg/ℓ CN solutions even with the degree of oxidation occurring under these test conditions.

Comparison of Collectors--

Comparison of the amines used indicates that the primary amine, 12-D, was more effective than the quaternary amine, A336, above pH 7. It was observed that the froth volume and froth stability were good over all pH ranges with 12-D. However, with A336 very little froth was obtained above pH 7. In addition, this froth was very unstable. The lower recovery obtained with the quaternary amine probably is due to the lack of a suitable froth. This may be explained on the basis of a reduced concentration of quaternary amine in solution which would act as a frother. The quaternary amine probably is more strongly adsorbed to the negatively charged precipitates than the primary amine due to a more negative free energy change. The change in free energy of collectors is the result of several contributions (23). One contribution that is readily distinguishable is the free energy decrease which accompanies the removal of the hydrocarbon chains from water. This free energy change is 1.1 kT per CH_2 group, where k is the Boltzmann constant and T is the absolute temperature. The A336 has approximately 24 CH_2 groups. The 12-D has only 11 CH_2 groups. Thus the change in free energy of adsorption due to hydrocarbon chain length will be more negative for the quaternary amine. The

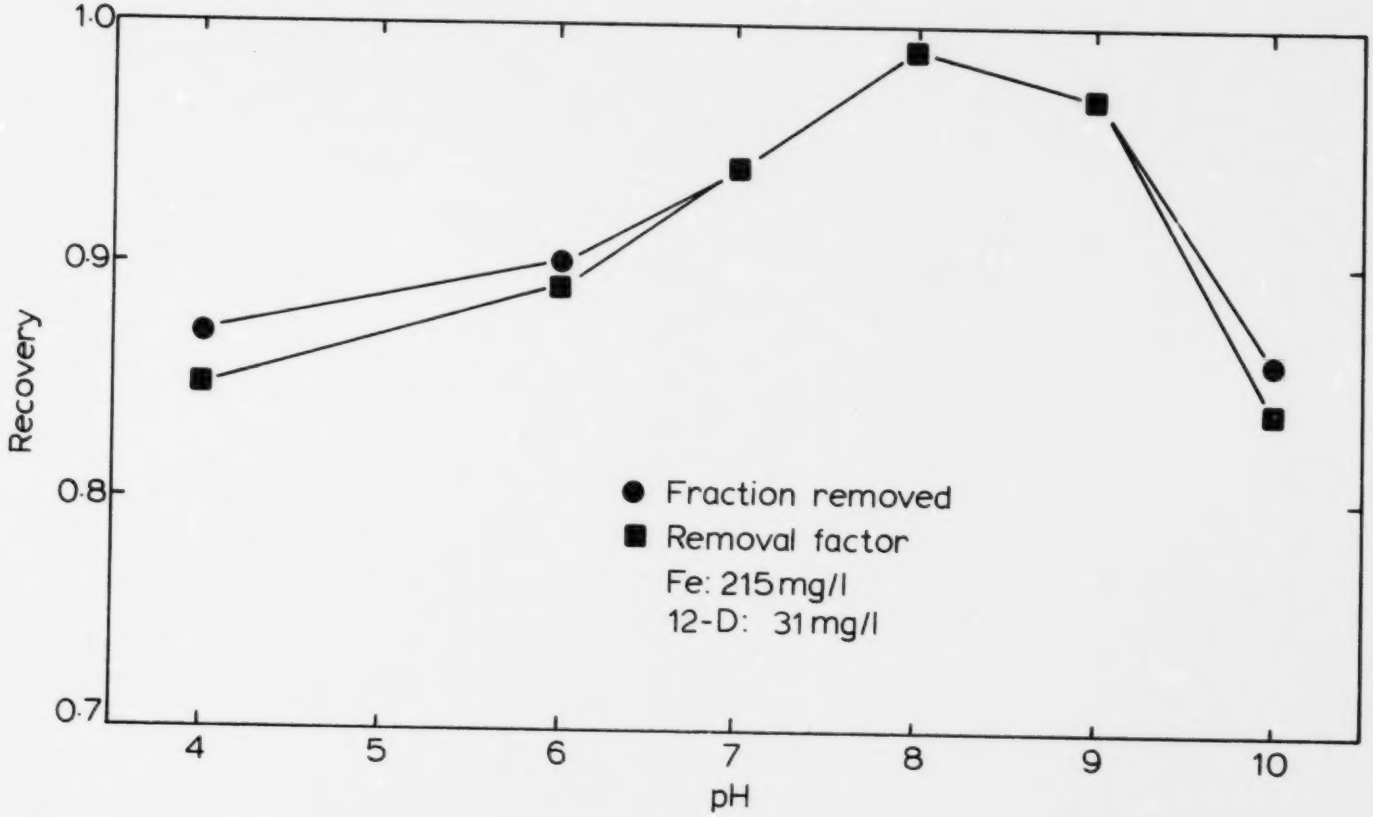

Fig. 6. The effect of pH on cyanide recovery from KCN-NaCl solutions using collector 12-D.

result is that the equilibrium concentration of quaternary amine in solution is too low to be an effective frother. Since the present work was directed toward precipitate flotation, and the primary amine considerably less expensive, no further work was done with the quaternary amine.

Frother Addition--

An experiment was run to study the effect of amine addition and frother addition on recovery from 100 mg/ℓ free cyanide solution containing 5000 mg/ℓ NaCl at pH 8. Iron addition was 215 mg/ℓ and reaction times, conditioning times and flotation times were each five minutes. The collector used was 12-D at levels of 12.0, 24.0, and 31.0 mg/ℓ. The results as shown in Table 7 indicate that recovery decreased from 99% to 94% as the collector addition decreases from 31 to 12 mg/ℓ without frother addition. With addition of frother at the lowest level of collector (12 mg/ℓ), the recovery increased from 94% to 97%. The same recovery, 97% was obtained with twice as much amine (24 mg/ℓ) both with and without frother. This indicates that the addition of a frother may help in reducing amine requirements for iron cyanide precipitate flotation.

TABLE 7. RECOVERY AS A FUNCTION OF AMINE CONCENTRATION AND FROTHER ADDITION

Run	12-D mg/ℓ (mM)	MIBC	Fr	RF
44	31(.13)	0	.99	.99
46	24(.10)	0	.97	.97
47	12(.05)	0	.94	.94
48	24(.10)	20(.20)	.97	.97
49	12(.05)	20(.20)	.97	.97

100 mg/ℓ Total CN (added as KCN)
215 mg/ℓ Iron
pH 8.0

Coke Plant Liquors

A drum of intercepting sump water (I.S.W.) and a drum of crude (or waste) ammonia liquor (C.A.L.) were obtained from the Republic Steel Corporation plant in Cleveland, Ohio. The C.A.L. was dark colored and had a strong odor due to the high concentrations of ammonia and phenol. The total cyanide content was 10 mg/ℓ. The I.S.W. was a dirty brown color and contained 89 mg/ℓ total cyanide.

I.S.W. Liquors - Effect of pH--

Since the work on synthetic solutions showed that pH was the most important variable, a series of tests were run on the I.S.W. at various pH levels. Test conditions were 24 mg/ℓ of collector 12-D, 200 mg/ℓ of iron and reaction times, adsorption times, and flotation times of 15, 10, and 5 minutes respectively. The iron addition was equivalent to 180% mole excess over

cyanide. The original iron content of the solution was unknown.

At pH 5 it required almost four minutes of reaction time before the solution turned a deep blue color. The rate of appearance of the blue color gives a qualitative measurement of the rate of iron cyanide precipitation. With the synthetic solutions the deep blue color formed immediately after the $FeSO_4 \cdot 7\ H_2O$ was added. Apparently something in the I.S.W. is hindering the iron cyanide precipitation reaction. At the higher values of pH, the floc-like green precipitates formed at a rate similar to that in the synthetic solutions. The oxidation of the ferrous ion did not appear to be hindered in the I.S.W. Organic impurities are known to hasten oxidation reactions (17). Results, as shown in Figure 7, indicate that the recovery reaches a maximum of 91% at about pH 7. It should be noted that at pH 8 the recovery of cyanide from the I.S.W. is significantly lower than from synthetic solution at this same pH. This is probably because of the slower rate of iron cyanide precipitation. The longer time required for iron cyanide precipitation allows more time for the oxidation of ferrous iron to occur. The oxidation of ferrous iron will deplete the amount of ferrous iron available for complexing with the cyanide. At pH 8 the oxidation rate of ferrous ion in solution is limited only by the diffusion of oxygen into the solution (17). Thus a slower rate of iron cyanide precipitation will reduce the recovery of cyanide for a limited excess amount of ferrous iron. It was also noted that in the tests done at pH 7 or greater, the underflow was clear but yellow in color. The color may be due to ferric oxide colloids which tend to be stabilized by organic matter (17). The colloids could be removed by sand filtration (17).

Reaction Time

In order to design a reaction vessel with the proper retention time, the overall rate of the complexing and precipitation reactions (the reaction time) must be known. Consequently a series of tests were run on I.S.W. at pH 7 as a function of reaction time; the other test conditions were the same as in the preceding section. The results, as shown in Figure 8, indicate that a 5 minute reaction time is sufficient and that the recovery (over 90%) is essentially the same for reaction times of 5 to 30 minutes. The recovery dropped to about 80% at a reaction time of 45 minutes. It is possible that the prolonged agitation resulted in a reduction of the flocs to very fine particles which did not float. A mass balance on this test gave a total cyanide content of 74 mg in the overflow and 14 mg in the underflow. The difference of 1 mg from the feed of 89 mg could be a result of stripping of some HCN in the gas phase or could be experimental error.

C.A.L. Liquor

The C.A.L. liquor was floated at pH 7 with 24 mg/ℓ of collector 12-D, 200 mg/ℓ iron, and reaction, adsorption, and flotation times of 15, 5, and 5 minutes respectively. This resulted in a cyanide recovery of about 40%. The feed liquor was reduced from 10 mg/ℓ to 6 mg/ℓ cyanide. The addition of amine resulted in additional coagulation. These coagulated solids then reported in the froth product. The froth product was a very dark brown.

Another test was done with the C.A.L. using similar conditions except

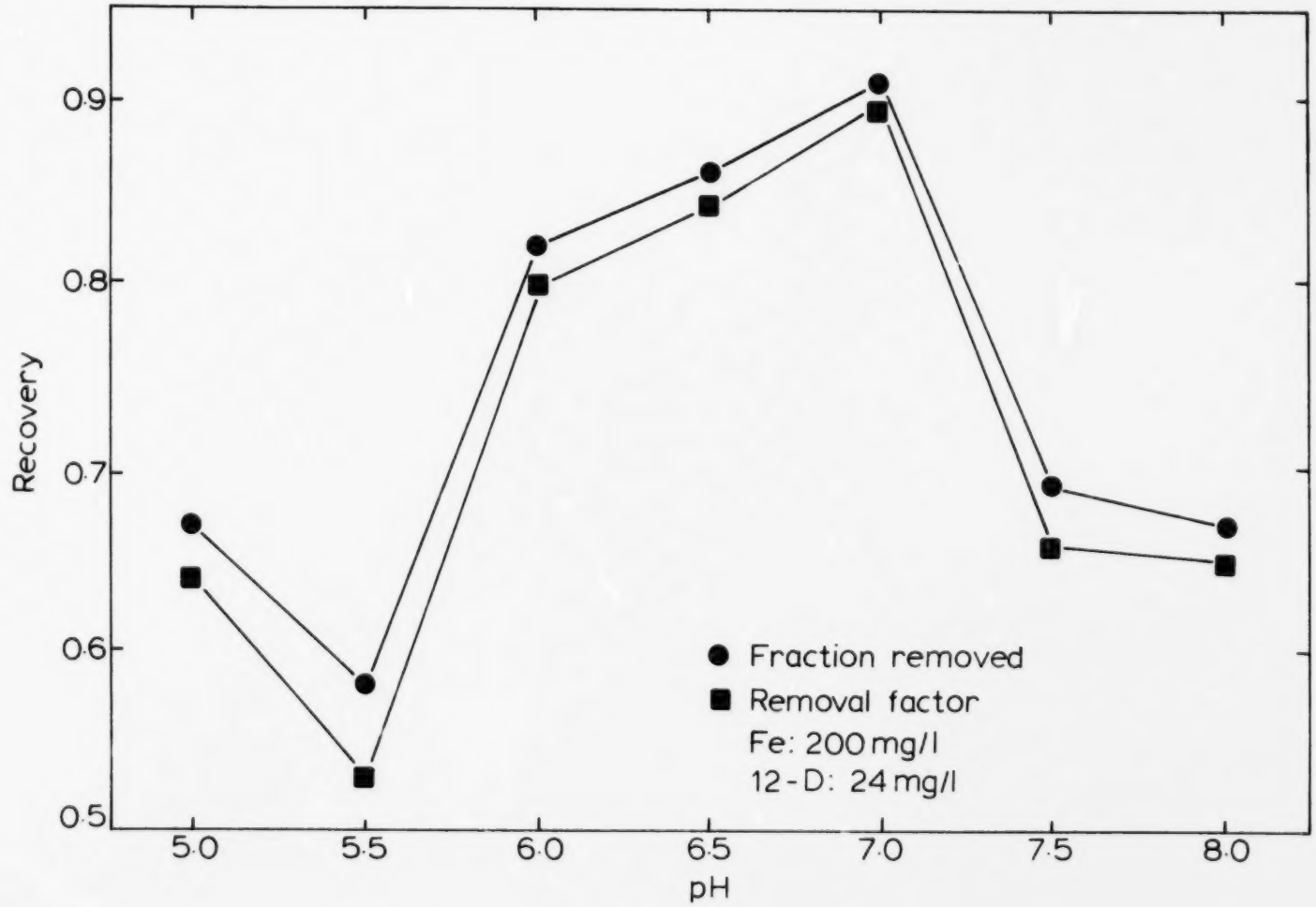

Figure 7. The effect of pH on cyanide recovery from coke plant intercepting sump water.

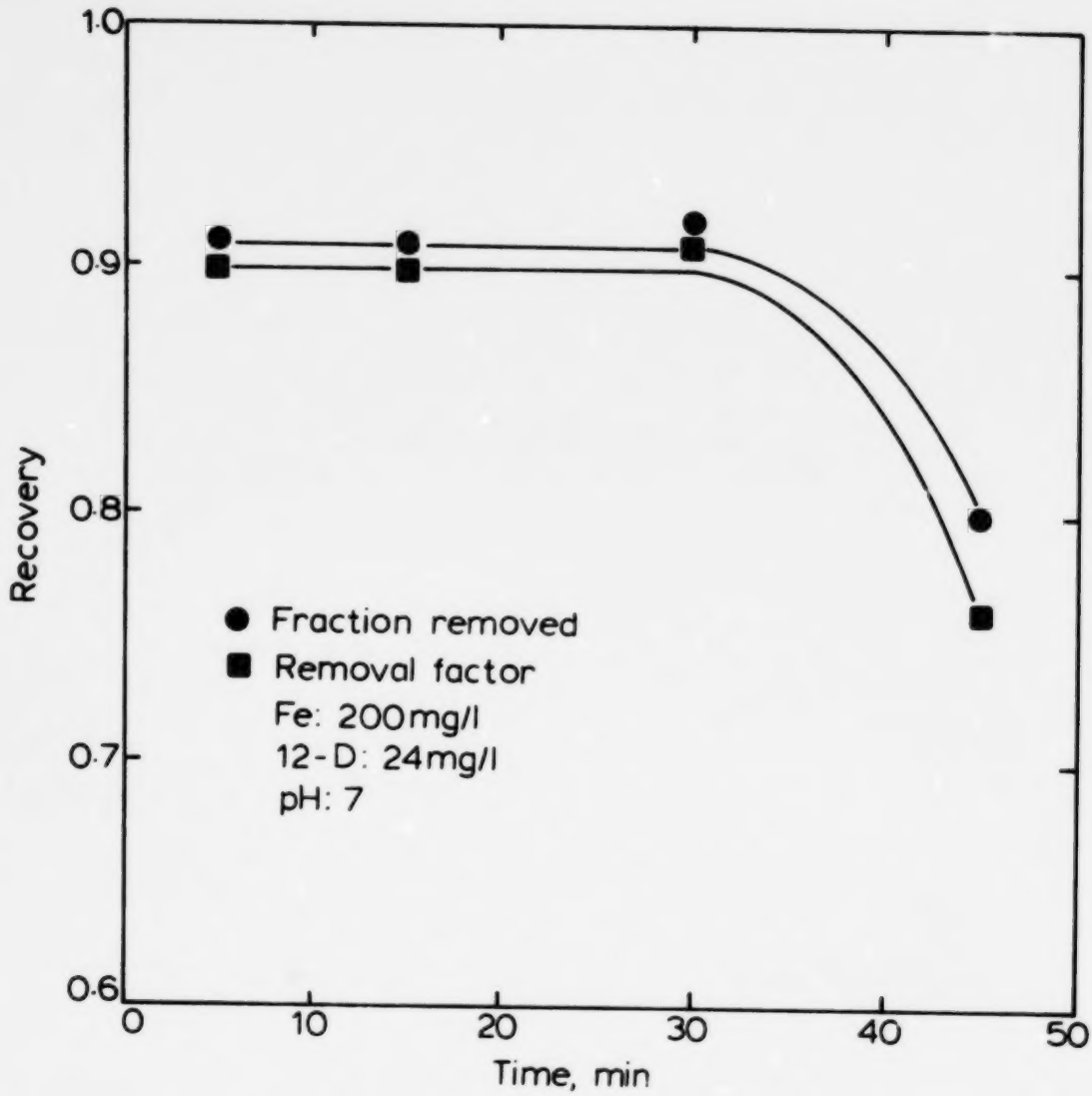

Figure 8. The effect of reaction time on cyanide recovery from coke plant intercepting sump water.

that no amine was used. The cyanide level in the underflow was 4 mg/ℓ. The C.A.L. foamed very well without the 12-D. The underflow contained slightly more suspended material than the first test. Apparently the C.A.L. contains enough oil and other surface active organic material to make many of the precipitates surface active. Schroeder (3) while doing semi-pilot plant work with a dissolved gas flotation unit reported similar results. He stated that 40 mg/ℓ of debenzolized wash oil proved to be effective inexpensive replacement for surfactants. The debenzolized wash oil was obtained from the light oil refining process in a by-product coke plant.

These results indicate that a single stage batch flotation process will:

(i) remove over 98% of the cyanide from synthetic cyanide solutions.

(ii) remove 90% of the cyanide from plant liquors with cyanide concentrations of approximately 90 mg/ℓ. If the same percentage recovery can be achieved at feed concentrations of the order of 50 mg/ℓ the higher of the two effluent limitations can be met.

(iii) has the potential of a primary process for bulk removal of cyanide and possibly a process for meeting effluent standards if additional flotation stages are added. In addition, the underflow is relatively clear indicating possible removal of some of the other contaminants.

Disposal of the Flotation Concentrate

Any process which will concentrate the cyanide waste material should be followed by a process which will detoxify the concentrate. The Wetox® process has proven successful in this respect on coke oven gas scrubbing liquors (24). The process is based on the fact that organic material in aqueous solutions can be oxidized to any desired extent under pressure, at temperatures of 150-350°C. During the process the cyanide is hydrolized via the following reaction:

$$CN^- + 2H_2O \text{ ------ } NH_3 + HCOO^-$$

Any thiocyanate that is present is oxidized as follows:

$$SCN^- + 2O_2 + 2H_2O \text{ ----- } NH_4^+ + CO_2 + SO_4^{-2}$$

The Center for Waste Management Programs at Michigan Technological University has Wetox® equipment. Using their equipment a batch experiment was done with conditions similar to those described in the literature. The test conditions and the test sample are described in Table 8. No detectable cyanide was found in either the product solution or product gases.

The reaction product of this oxidation process is essentially solid iron oxide. This waste product was tested for EP Toxicity by the OSW Extraction Procedure (25) and found to be well below the allowable maximum contaminant levels. Results are shown in Table 9.

TABLE 8. WETOX® OF FERROCYANIDE WASTES

Test Sample	(1) 1.0 liter tap water (2) 5.4 gm $K_4Fe(CN)_6$(2000 mg ^-CN) (3) 10.7 gm $FeSO_4 \cdot 7H_2O$ (4) 1.0 gm Dodecylamine acetate
Test Conditions	(1) 1 gal. reactor 2.791 of air @ 200 psig 50°F (2) Heated to 550°F, final pressure 1350 psig (3) Reaction time 60 minutes (4) Quench cool
Results:	Iron oxidized to a red oxide Remaining Cyanide* In liquor <1 mg/ℓ In off gases <0.5 mg

*Titration Method

TABLE 9. ANALYSIS OF SOLID WETOX® WASTE PRODUCT

EPA Hazardous Waste Number	Contaminant	Maximum Allowable Concentration Milligrams per liter (25)	Concentration Found Milligrams per liter
D004	Arsenic	5.0	0.00
D005	Barium	100.0	0.13
D006	Cadmium	1.0	0.00
D007	Chromium	5.0	0.00
D008	Lead	5.0	0.00
D009	Mercury	0.2	0.03
D010	Selenium	1.0	0.00
D011	Silver	5.0	0.03

It appears that the Wetox® process is a technically feasible method of destroying cyanide waste. More tests are needed to confirm process performance and the design variables. An economic feasibility study could then be done to compare Wetox® with other existing processes.

ION EXCHANGE

Removal of cyanide from synthetic solutions containing 25 mg/ℓ cyanide as ferrocyanide plus 5000 mg/ℓ chloride as NaCl at pH 7.6 was studied using Amberlite IRA-958. Three successive adsorption and elution tests (Tests 6, 7, and 9) were run on the same resin at a flow rate of 19.4 BV/hr. and three additional tests (Tests 10, 11, 12) on a second resin column at a flow rate of about 16.0 BV/hr. Results of these tests are shown in Table 10.

TABLE 10. ION EXCHANGE OF FERROCYANIDE

Test	Cycle	Flow Rate BV/hr	Volume to[1] Breakthrough BV	Total Volume Treated BV	Final Effluent mg/ℓ CN	Composite Effluent[2] mg/ℓ CN
New resin						
6	1	19.3	420	535	0.85	0.18
7	2	19.4	303	343	0.40	0.06
9	3	19.4	383	465	2.50	0.90
New resin						
10	1	15.9	493	543	0.43	0.08
11	2	16.0	510	525	0.28	0.10
12	3	15.8	618	708	1.70	0.05

[1]Breakthrough volume at point where effluent contains 0.25 mg/ℓ CN

[2]Composite effluent analysis at termination of test - mg/ℓ CN

Excellent adsorption was obtained at both flow rates. Breakthrough volumes are greater at the slower flow rate as would be expected. These breakthrough volumes are of the order 400 BV at 19.4 BV/hr and 500-600 BV at 15.9 BV/hr. It should be noted that even though the tests were run past the breakthrough point the composite barrens, with one exception, were below 0.25 mg/ℓ CN.

In cycle 1 (T-6) the elution was carried out at pH 9.0 and the material balance indicated incomplete elution. This resulted in decreased adsorption in the cycle 2 (T-7) in which the breakthrough volume decreased. Upon elution of Test 7 at pH 10.2 the amount of cyanide eluted was greater than the amount adsorbed in that cycle indicating removal of some of the cyanide not eluted in the previous cycle. In the cycle 3 (T-9) the adsorption increased indicating that the higher pH used in elution of the previous cycle removed some of the previously non-eluted cyanide. Elution of cycle 3 (T-9) at pH 12.2 again resulted in a net gain in the material balance showing that elution at pH 12.2 was more effective than elution at pH 10.2.

A series of three consecutive cycles were then run on a new resin column (T-10, T-11, T-12) at a flow rate of about 15.9 BV/hr with successive elutions at pH 12.2. Excellent adsorption was obtained in all three cycles with breakthrough volumes of 525-700 BV. Composite barrens were all below 0.25 mg/ℓ CN. Material balances showed that essentially all the adsorbed cyanide was eluted in each cycle. Elution was essentially complete in 8 BV and over 90% of the cyanide was removed in the first 4 BV. It is of interest to note that even in the cases where elution was incomplete (T-6, 7, 9) the next adsorption cycle showed no bleed-through of cyanide in the early effluent fractions.

Although no tests using recycled eluate were performed, it should be possible to precipitate the ferrocyanide as the iron ferrocyanide and recycle the salt solution. The effectiveness of this process on plant liquors would have to be determined because of the presence of other anions, principally thiocyanate in the liquors.

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SECTION 6

RESULTS OF CONTINUOUS FLOTATION TESTS

GENERAL PROCEDURES

The following work was carried out at the Colorado School of Mines under the direction of Dr. D. J. Spottiswood. In this phase Aliquat 336 (A-336) was used as the surfactant followed by the addition of ferrous iron. Initial tests to determine amine-ferrocyanide stoichiometry involved batch extraction tests using carbon tetrachloride as the amine solvent. Batch tests were then run by dispersing the amine in the aqueous cyanide solution. This resulted in formation of a wax dispersion which was difficult to separate from the solution. Addition of ferrous iron to the dispersion resulted in rapid precipitation of the amine-ferrocyanide complex. This system of amine plus ferrous iron was then used in a continuous column flotation system. Details of each phase of this work are given below:

Two-Phase Batch Extraction Tests --

Extraction tests were carried out in separatory funnels to determine the stoichiometric ratio of amine to ferrocyanide. The results of extracting a 100 mg/ℓ CN solution of ferrocyanide with the amine (using CCl_4 as the diluent) are shown in Figure 9. The extent of extraction is given by the removal factor (RF) as defined in Section 5. Regression analysis of these results indicates a stoichiometry of approximately 3.5:1. The theoretical stoichiometry of the extraction product of amine (+1) and ferrocyanide (-4) is 4:1.

Batch Extraction Tests --

A second series of tests were carried out to determine the extent of extraction using the amine as a dispersion in the aqueous solution of ferrocyanide. Using an amine addition of 4.5 moles amine to 1 mole ferrocyanide, a yellow, waxy precipitate would quickly form, but the solution would not clear for long periods of time, up to several days. In an attempt to increase the coagulation and precipitation rate, a number of possible additives and condition changes were screened. The addition of ferrous iron following reaction with the amine proved to be the best approach. The minimum concentration of Fe^{+2} (added as ferrous sulfate) required for rapid precipitation was 4.5×10^{-3} M (251 mg/ℓ). Extraction results are shown in Figure 10 for 10 mg/ℓ CN and 75 mg/ℓ CN solutions of ferrocyanide at various amine additions. Increasing the amine addition above an amine to ferrocyanide mole ratio of 3:1 did not materially affect the extraction.

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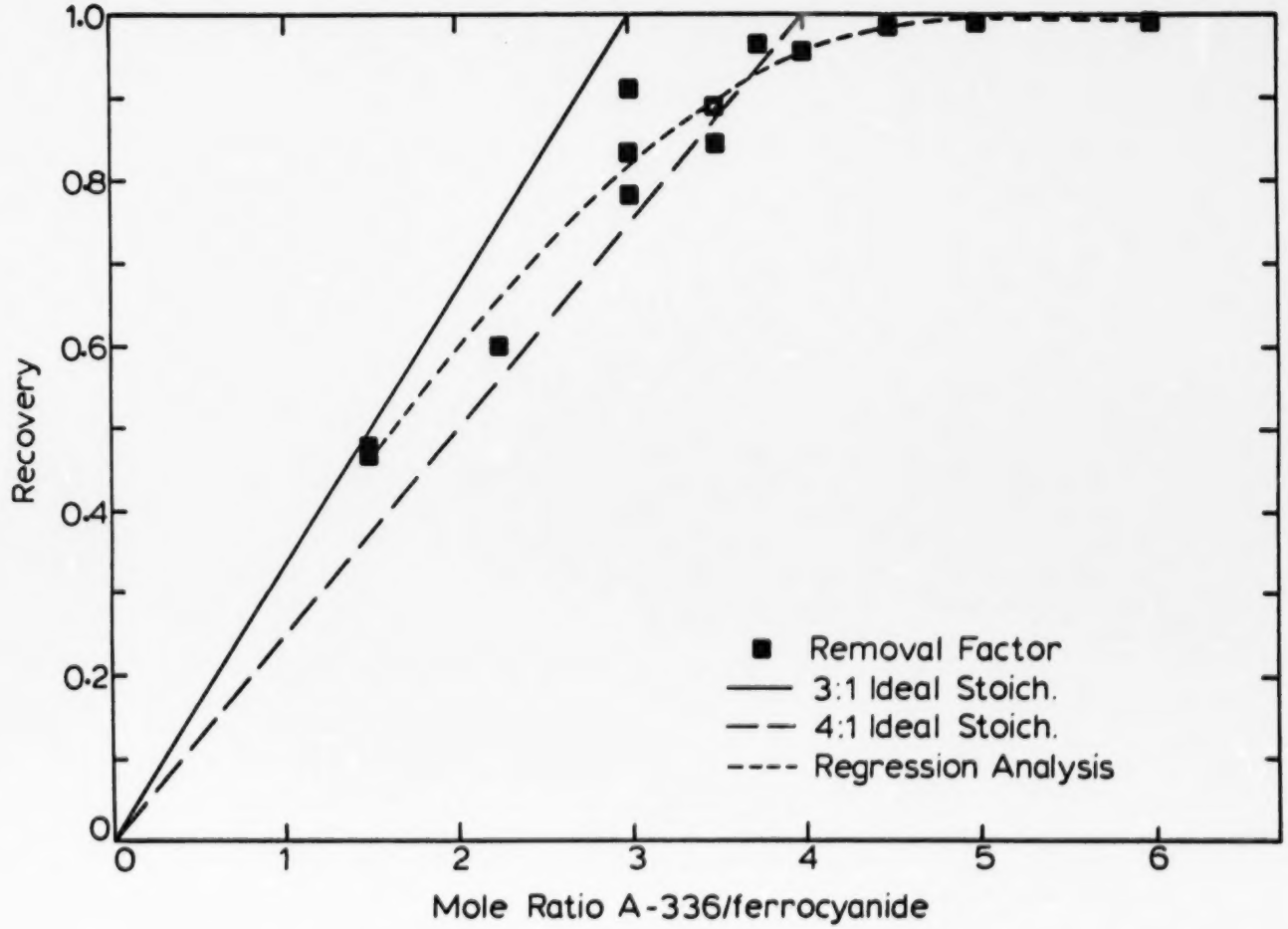

Figure 9. Removal of ferrocyanide in two-phase batch extraction tests.

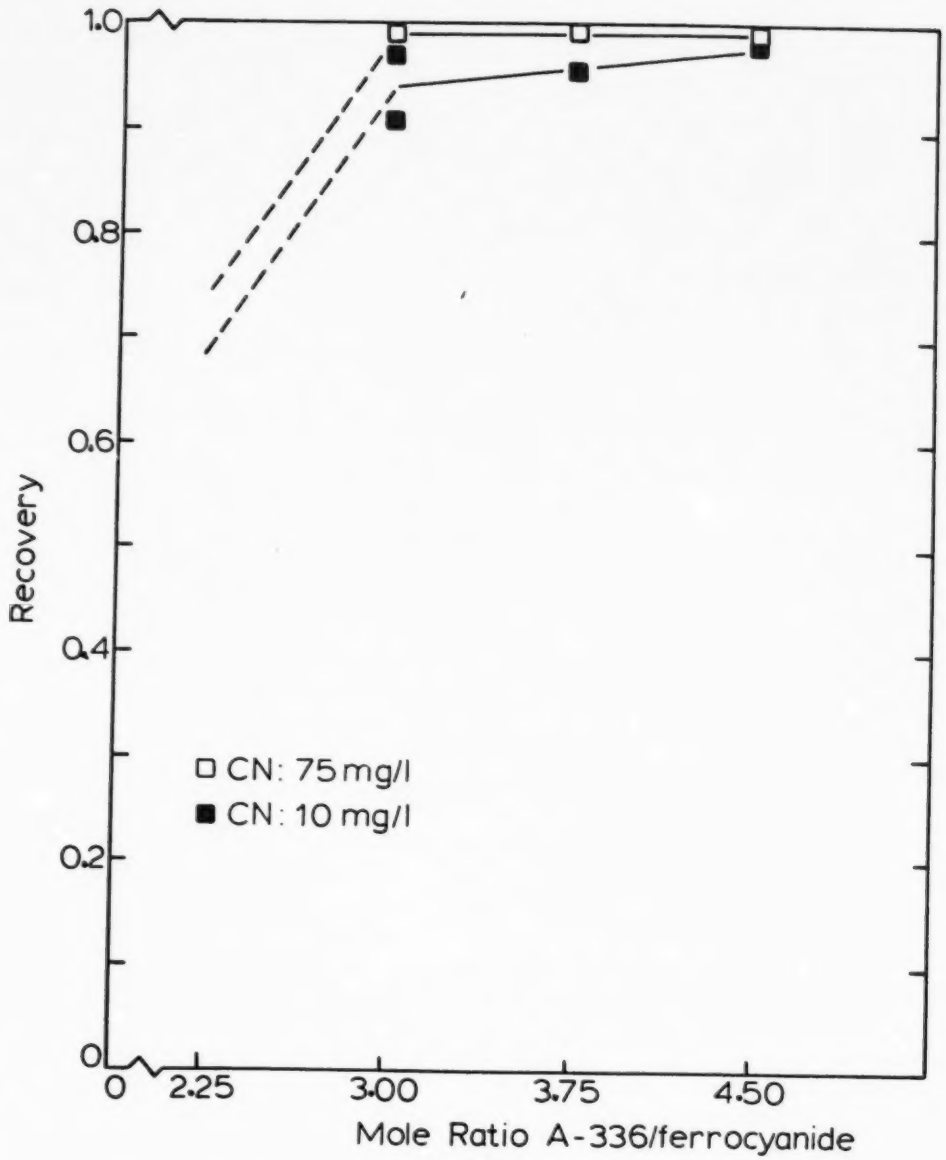

Figure 10. Effect of amine dosage with iron addition on removal of ferrocyanide in batch extraction tests.

The effect of feed concentration on cyanide recovery using an amine to ferrocyanide mole ratio of 3:1 plus iron is shown in Figure 11. Above a feed concentration of 25 mg/ℓ CN recoveries of approximately 98% were obtained. Below concentrations of 10 mg/ℓ CN no visible precipitate was obtained.

Continuous Column Flotation Tests --

A series of continuous flotation tests were carried out using the apparatus shown in Figure 12. Initial testing showed that a retention time of approximately 5 minutes was required for the amine-ferrocyanide reaction. An additional retention time of 1 minute was required following ferrous iron addition for precipitation to occur. Longer retention times were of no benefit in either reaction.

Column Operating Parameters --

The effect of column operating parameters using constant feed conditions (50 mg/ℓ CN as ferrocyanide, a 3:1 mole ratio of amine to ferrocyanide, and 251 mg/ℓ Fe^{+2}) is shown in Figures 13 through 15. Recoveries are given in terms of the removal factor (RF) and removal (R) where R is defined as the removal factor multiplied by the ratio of the underflow to feed volume flow rates. This assumes that the water carried over in the froth has the same concentration as the feed and thus amounts to a loss in recovery. As shown, the results indicate that over the range of operating conditions possible in a 1-inch diameter column, variations in feed flow rate, specific air rate, or retention time in the column (varied by changing column height) have only a slight effect on recovery.

Variations in Feed Concentration --

Column performance as a function of feed concentration is shown in Figures 16 and 17. Removal factors are relatively constant (about 0.9) over the concentration ranges tested but the removal (R) decreases with increasing feed concentration as indicated in Figure 16. The cyanide concentrations in the column effluent as a function of feed concentration are shown in Figure 17. The cyanide effluent limitations of 2.4 mg/ℓ and 5.1 mg/ℓ for the two operations described earlier are indicated by the dashed lines. These results indicate that:

(i) substantial removal of ferrocyanide can be achieved.
(ii) effluent limitations of 5.1 mg/ℓ cyanide can be met for feed solutions with concentrations less than 62 mg/ℓ cyanide and the lower limits of 2.4 mg/ℓ cyanide for feed solutions with concentrations less than 35 mg/ℓ cyanide.
(iii) the method has the potential, as a first stage process, of removing the bulk of the cyanide even if it cannot meet the effluent regulations.

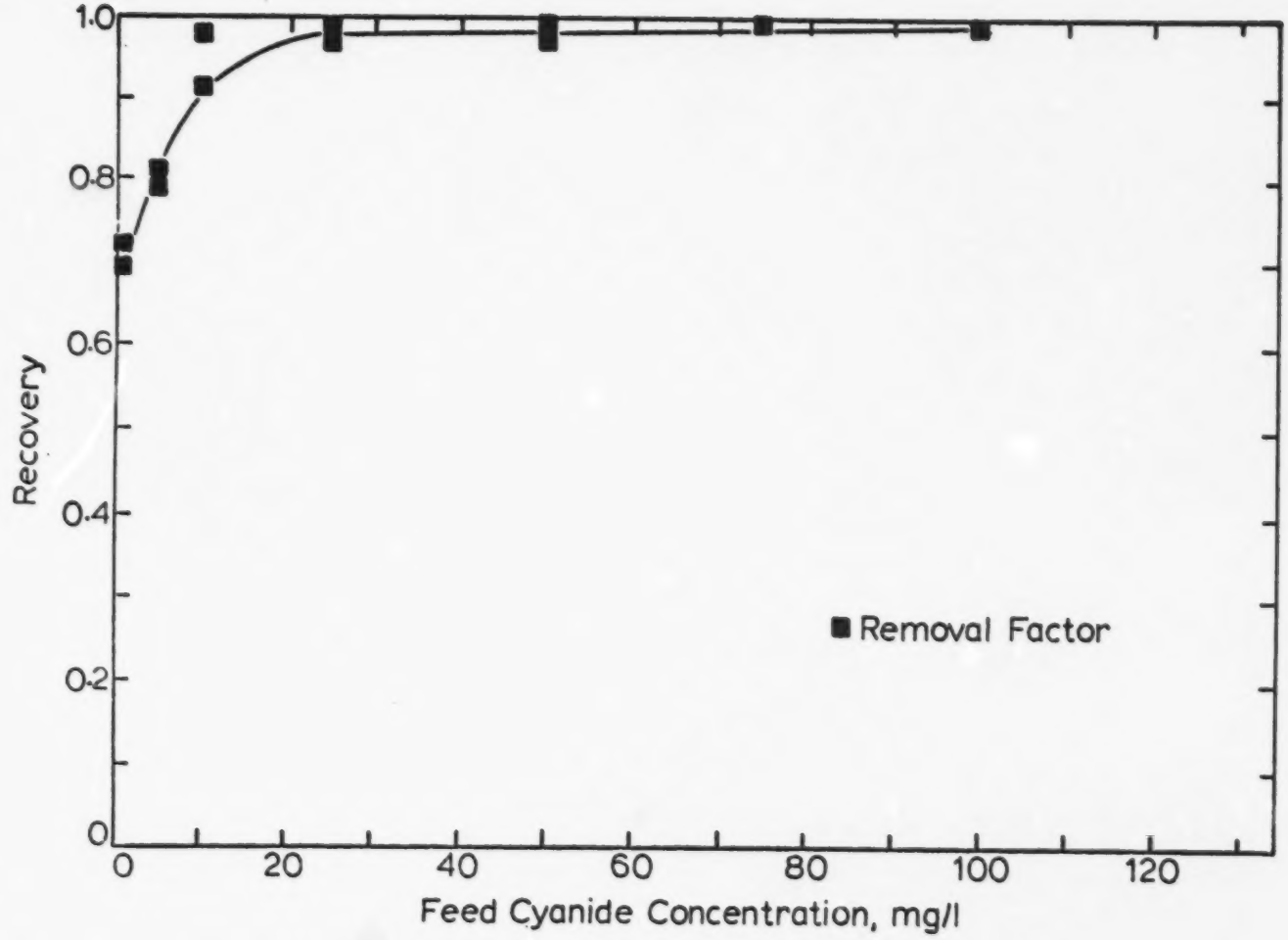

Figure 11. Effect of feed concentration on removal of ferrocyanide in batch extraction tests using A-336 plus iron.

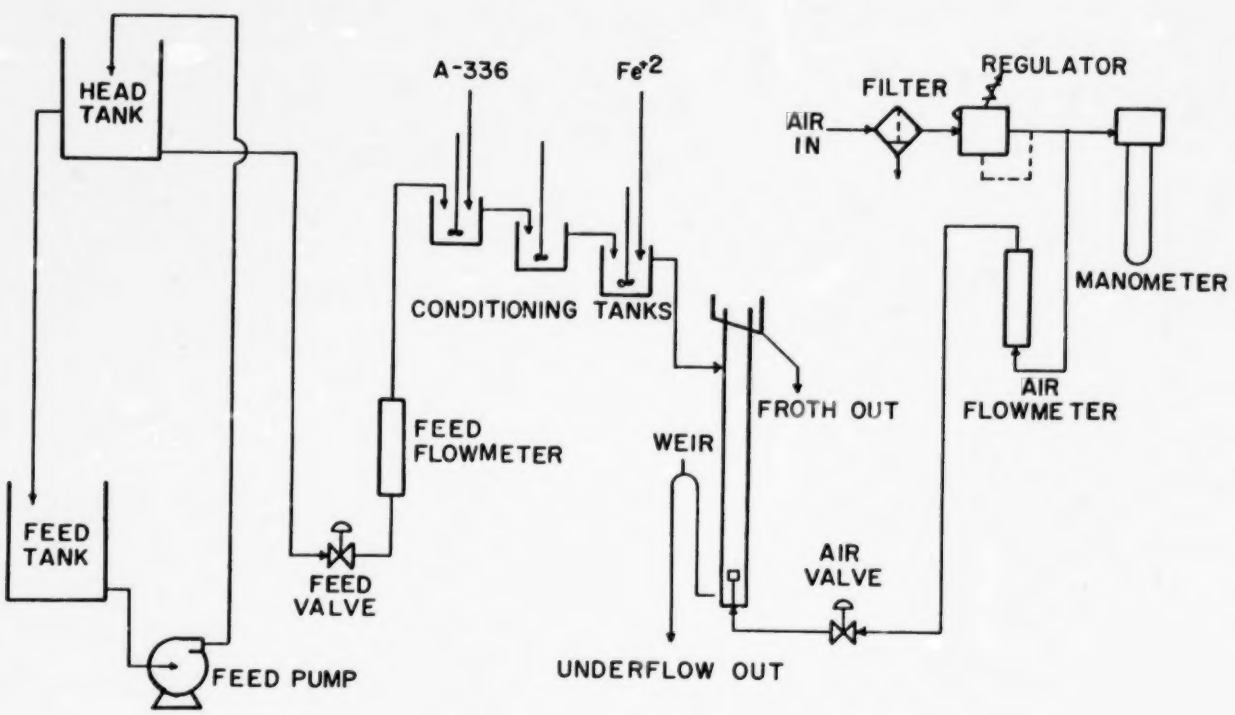

Figure 12. Schematic of continuous column flotation system.

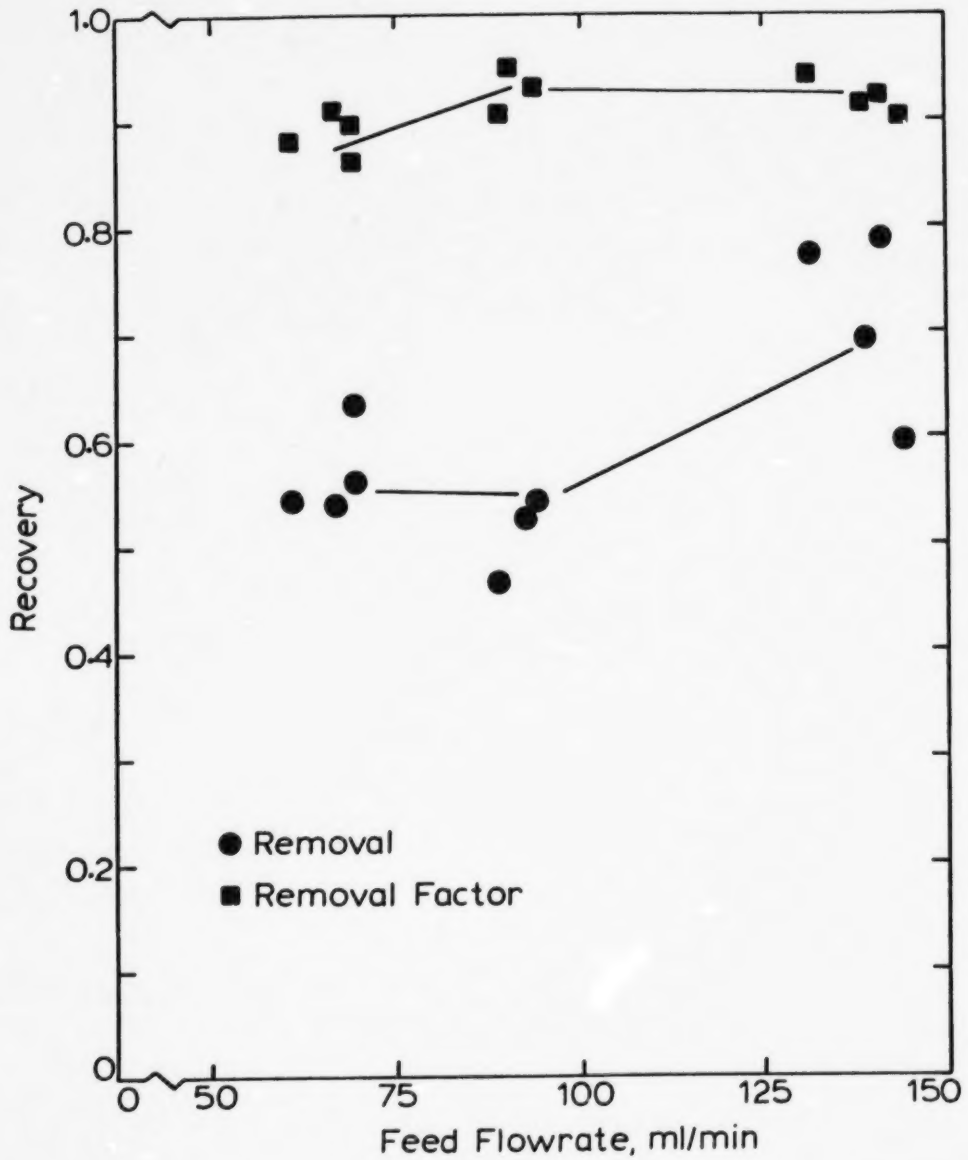

Figure 13. Performance of flotation column as a function of feed flowrate.

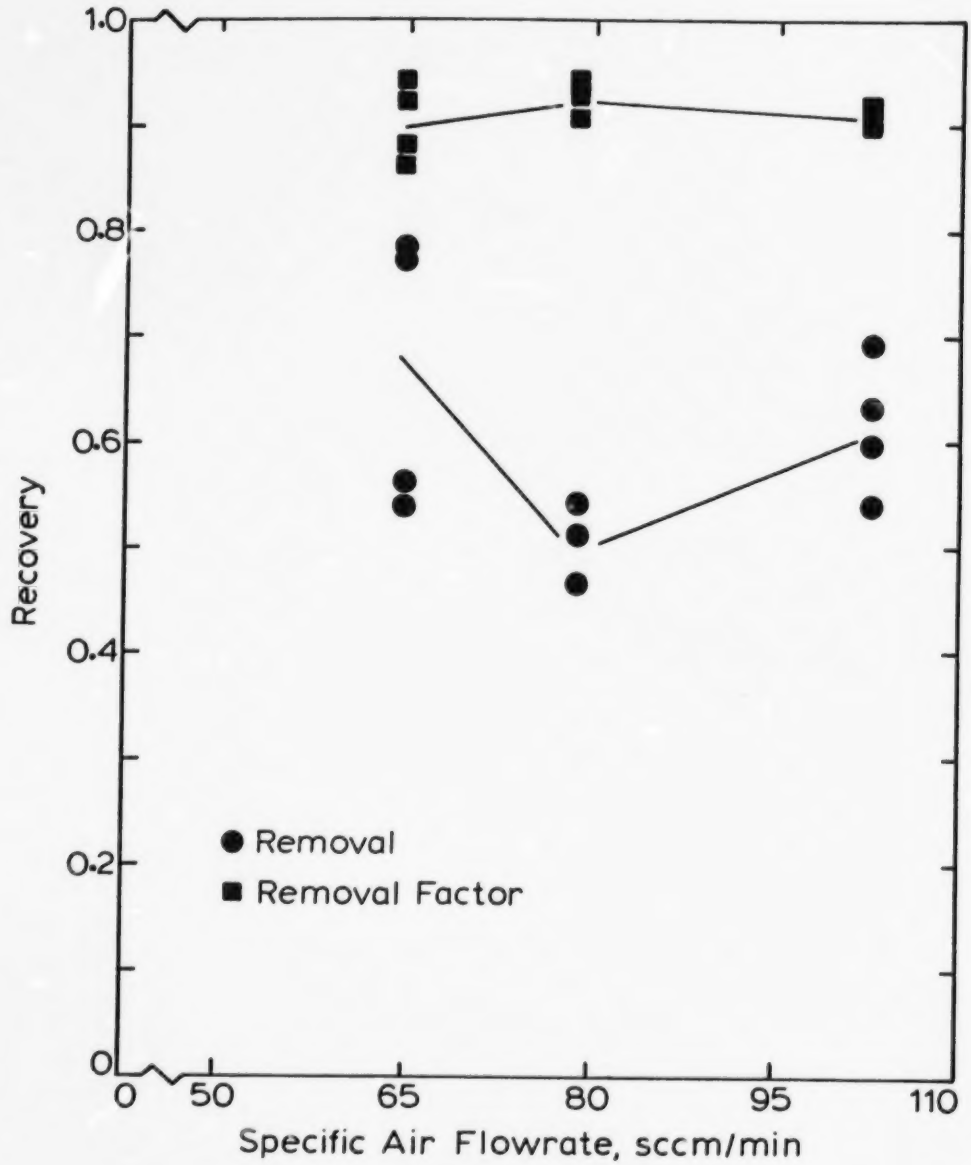

Figure 14. Performance of flotation column as a function of specific air flowrate.

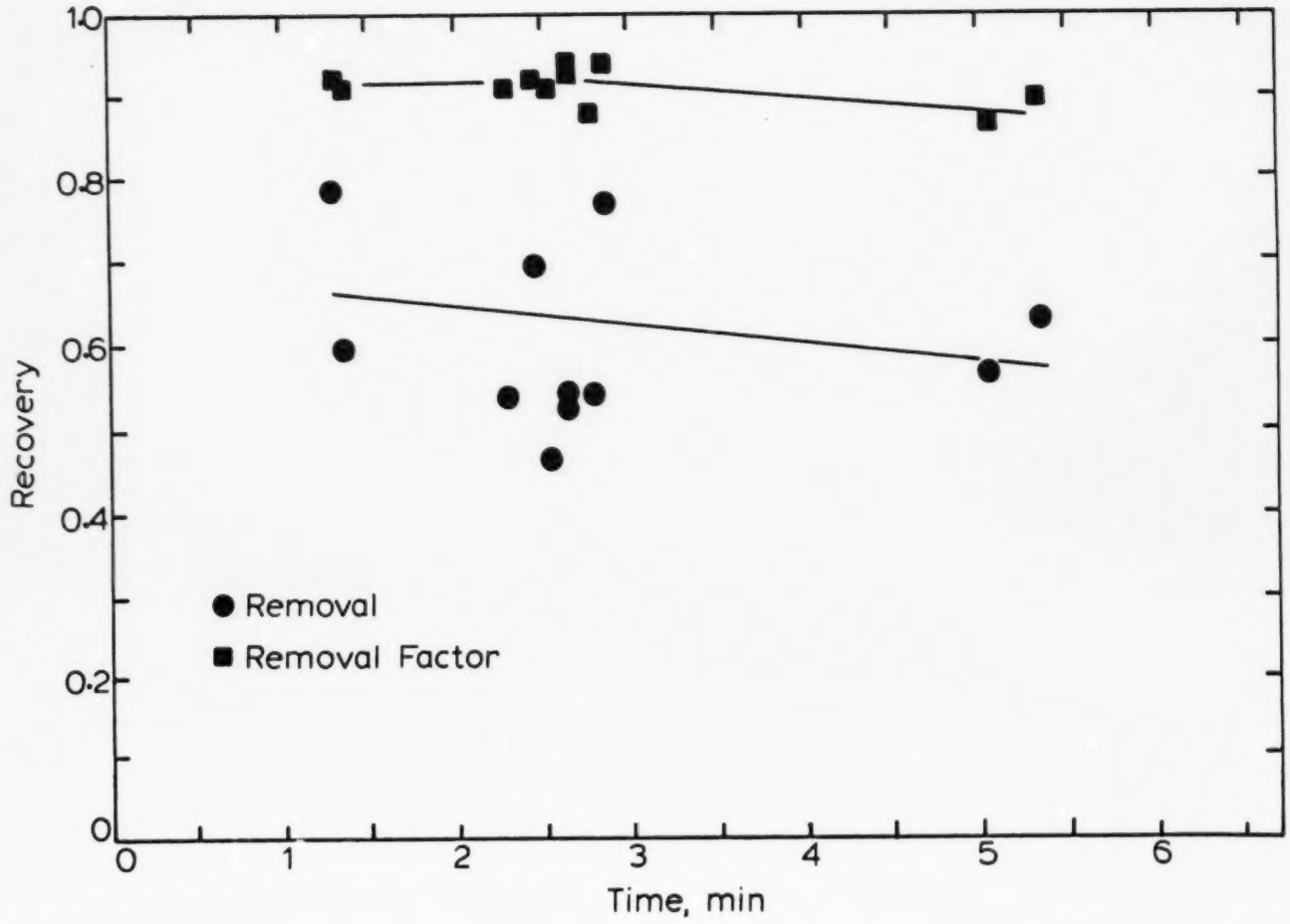

Figure 15. Performance of flotation column as a function of retention time.

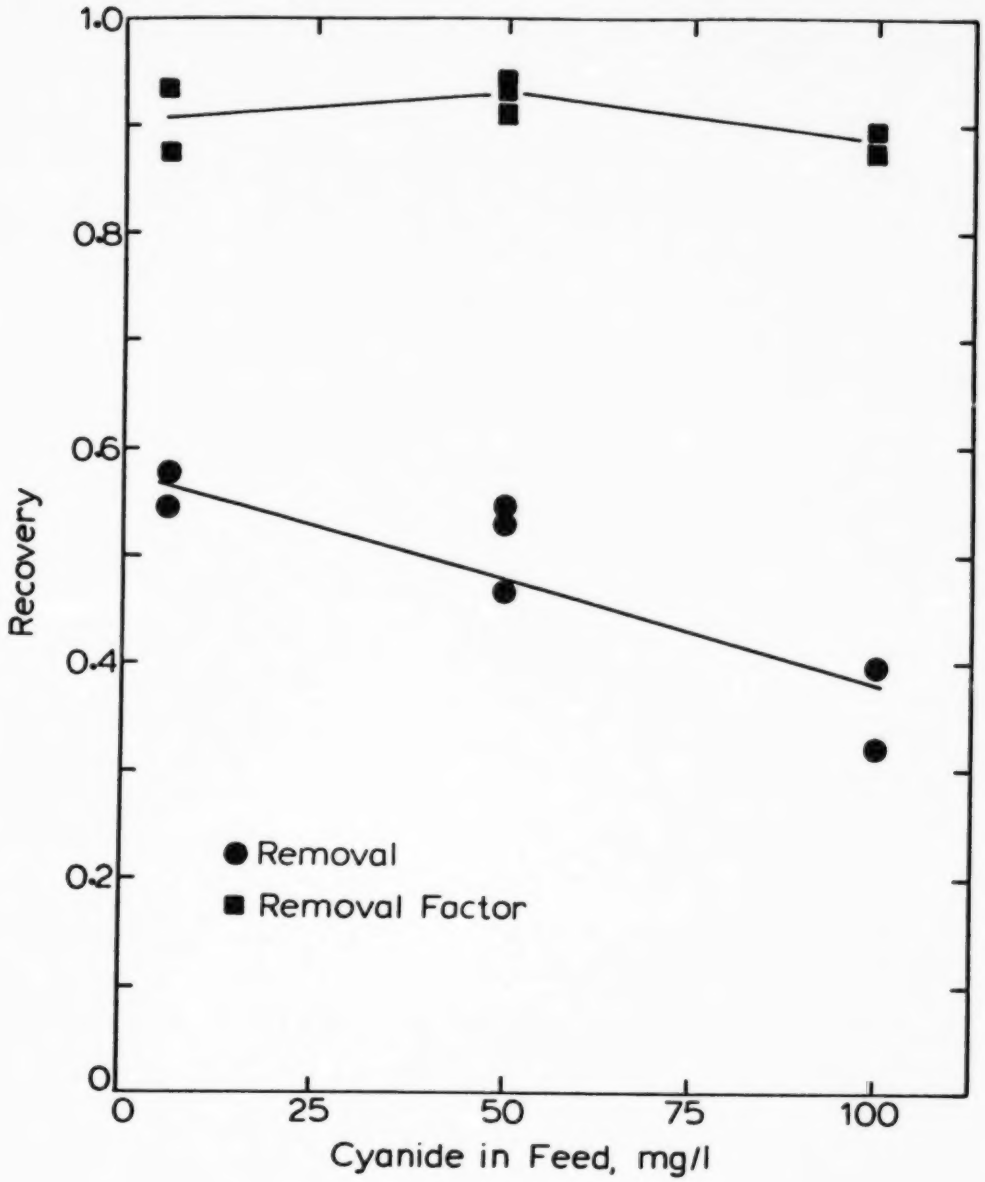

Figure 16. Performance of flotation column as a function of cyanide concentration in the feed.

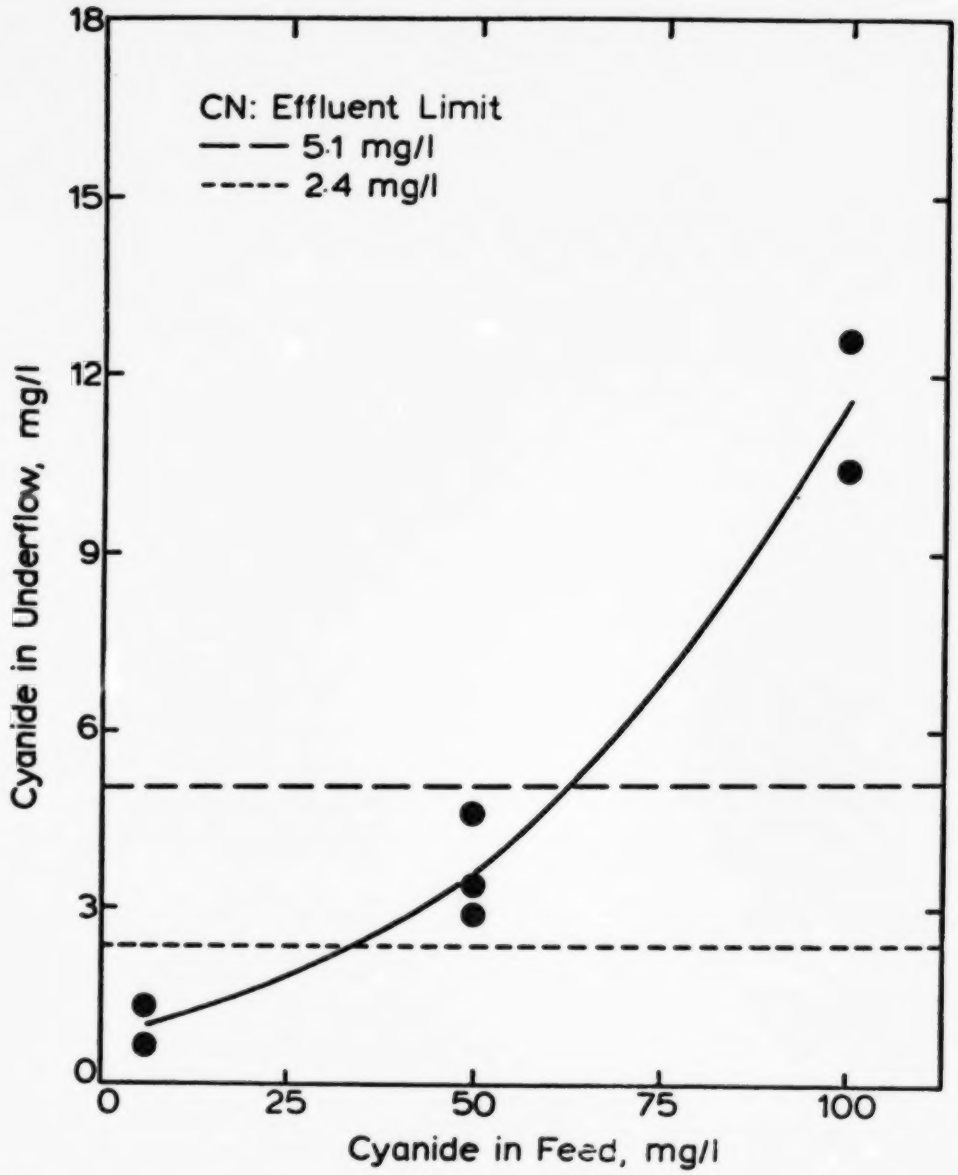

Figure 17. Effluent cyanide concentration performance of flotation column.

SECTION 7

ION FLOTATION OF IRON CYANIDE COMPLEXES

GENERAL PROCEDURES

This phase of the investigation centered on the determination of the feasibility of removing iron cyanide complexes by ion flotation. This process involves complexing the ionic cyanide species with a hydrophobic complexing agent to produce a neutral ion-pair complex capable of attaching itself to an air bubble. The organic iron cyanide complex could then be removed from the liquor as a froth product by flotation. Grieves and Bhattacharyya (26,27) have demonstrated that a cationic surfactant, ethylhexylammonium bromide, removed ferrocyanide in a batch foam process. In the present study the major effort was centered on the flotation of ferricyanide using a quaternary amine, tricaprylammonium chloride (Aliquat 336, General Mills) in a single stage continuous flotation column.

Complex Formation

In order to determine the ability of the amine to complex cyanide species, distribution tests were run using a chloroform solution containing 1% amine (by volume) and aqueous solutions of 2.0 mg/ℓ $Fe(CN)_6^{-4}$, 20.0 mg/ℓ $Fe(CN)_6^{-3}$, and 20.0 mg/ℓ CN^- respectively. Distribution coefficients (defined as the ratio of the concentration of the species in the organic phase to that in the aqueous phase) of the order of 15 to 19 for ferrocyanide, 40 to 70 for ferricyanide, and 20 to 26 for cyanide were obtained. The magnitude of these coefficients demonstrates that the amine extracts all of these species. This indicates complex formation and therefore the possibility of removal of the organic cyanide complexes by flotation.

Ion Flotation of Ferricyanide

All flotation tests were carried out in the continuous flotation column shown in Figure 1 using synthetic solutions of $K_3Fe(CN)_6$ containing 36.8 mg/ℓ $Fe(CN)_6^{-3}$.

The general flotation procedure was to disperse the amine in a small volume of feed solution and add this dispersion to the bulk of the feed in the conditioning tank. After a period of conditioning, usually 10 to 12 minutes, the feed solution was pumped through the column counter-current to the air flow and the froth product removed. Unless otherwise stated an air flow rate of 0.16 ℓ/min/cm^2 and a flotation time of 1.74 minutes was used.

The effectiveness of flotation was determined by the fraction removed, Fr, and by the removal factor, RF, as defined in Section 5.

Amine Concentration --

The overall reaction for complex formation is shown below:

$$3R_4N\ Cl + Fe(CN)_6^{-3} = Fe(CN)_6\ (R_4N)_3 + 3\ Cl^{-1}$$

Therefore the theoretical quantity of amine required to form a neutral complex would be at an amine to ferricyanide mole ratio of 3 to 1. Since this above reaction is an equilibrium reaction, some excess amine would be required to assure essentially complete reaction. Maximum recovery was achieved at an amine-ferricyanide ratio of 3.75 to 1 as shown in Figure 18. The neutral complex formed agglomerates into small wax-like particles and is recovered in the froth product. This amine usage is somewhat higher than the theoretical requirements as might be expected based on equilibrium considerations. At lower ratios the recovery decreases because of insufficient amine. At higher ratios the recovery also decreases. At the high amine ratios, emulsification occurs with a resulting decrease in recovery. This emulsification probably results from adsorption of excess amine on the wax particles with the hydrophilic end of the amine outward resulting in particle repulsion.

Many coke plant waste waters contain relatively high concentrations of chloride. Since the amine is in the chloride form, higher amine concentrations should be required in chloride solutions in order to drive the above reaction to the right. Flotation from solutions containing 5000 mg/ℓ chloride indicate that this occurs as shown in Figure 18. However, in these solutions the recovery does not reach a maximum but continues to increase with increasing amine addition. Emulsification does not occur in these chloride-containing solutions at these higher amine ratios.

Flotation Variables --

Recovery was found to increase rapidly with increasing conditioning time until a steady state was reached at approximately thirteen minutes as shown in Figure 19. It is possible that the conditioning time could be decreased by dissolving the amine in a water soluble solvent such as ethanol prior to addition.

Recovery also increases with increasing flotation time as shown in Figure 20. As indicated the recovery increased from 75% at a flotation time of 1.07 minutes to 83% at a flotation time of 2.3 minutes.

Increasing the air flow rate over a range of 0.08 to 0.22 $\ell/min/cm^2$ had only a minor effect on recovery as shown in Figure 21. The sharp decrease in the removal factor at the high air flow rate resulted from excessive carryover of solution into the overflow product.

Solution Variables --

Recovery remained essentially constant at about 82% over a ferricyanide concentration range of 30 to 70 mg/ℓ as shown in Figure 22. Below this range the recovery decreased to about 65% at 5.0 mg/ℓ ferricyanide.

The solution pH had little effect on recovery over a pH range of 4 to 7 as shown in Figure 23. The slight decrease in recovery above pH 7 probably results from increased competition for the amine by the hydroxyl ions.

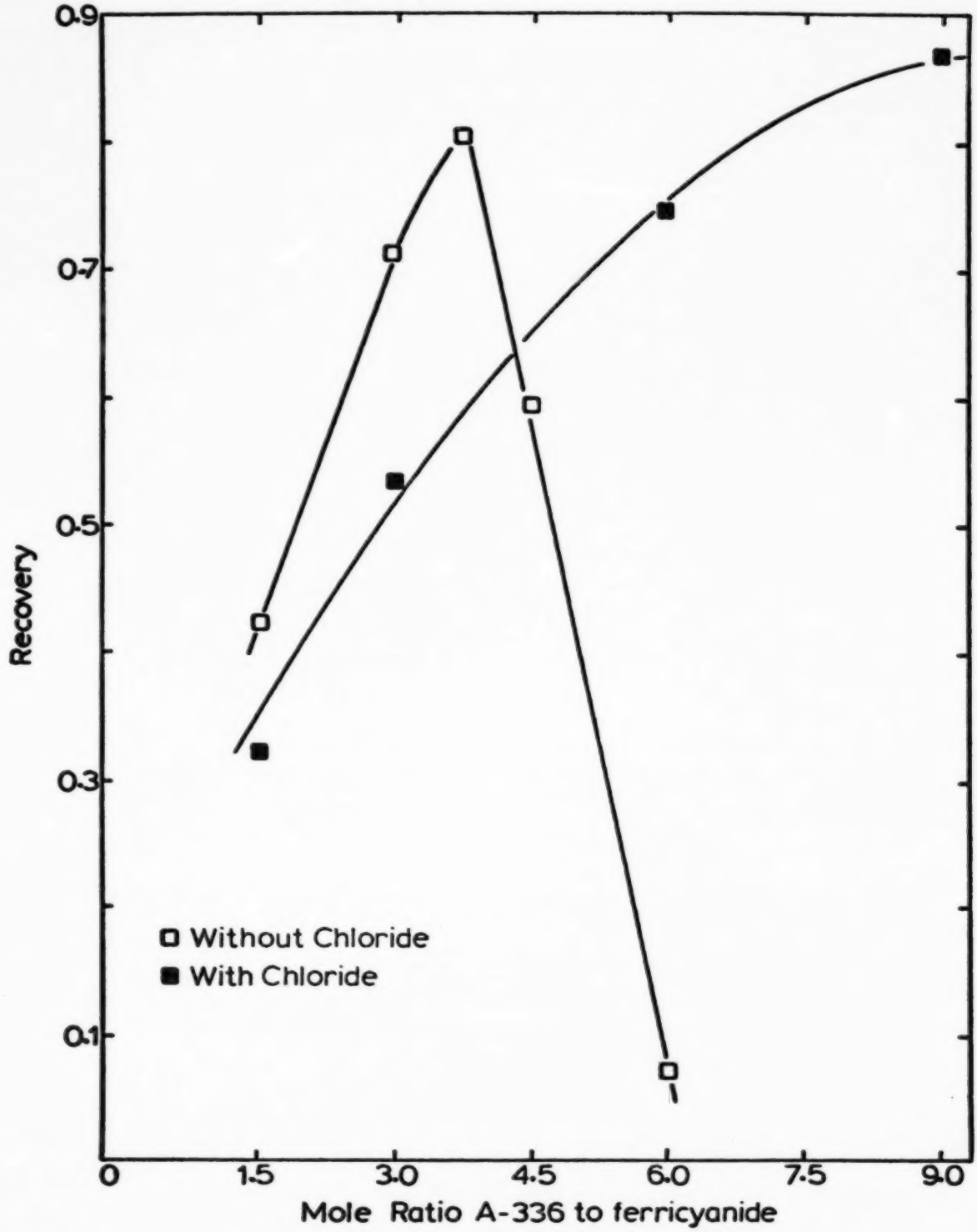

Figure 18. Cyanide recovery as a function of amine addition.

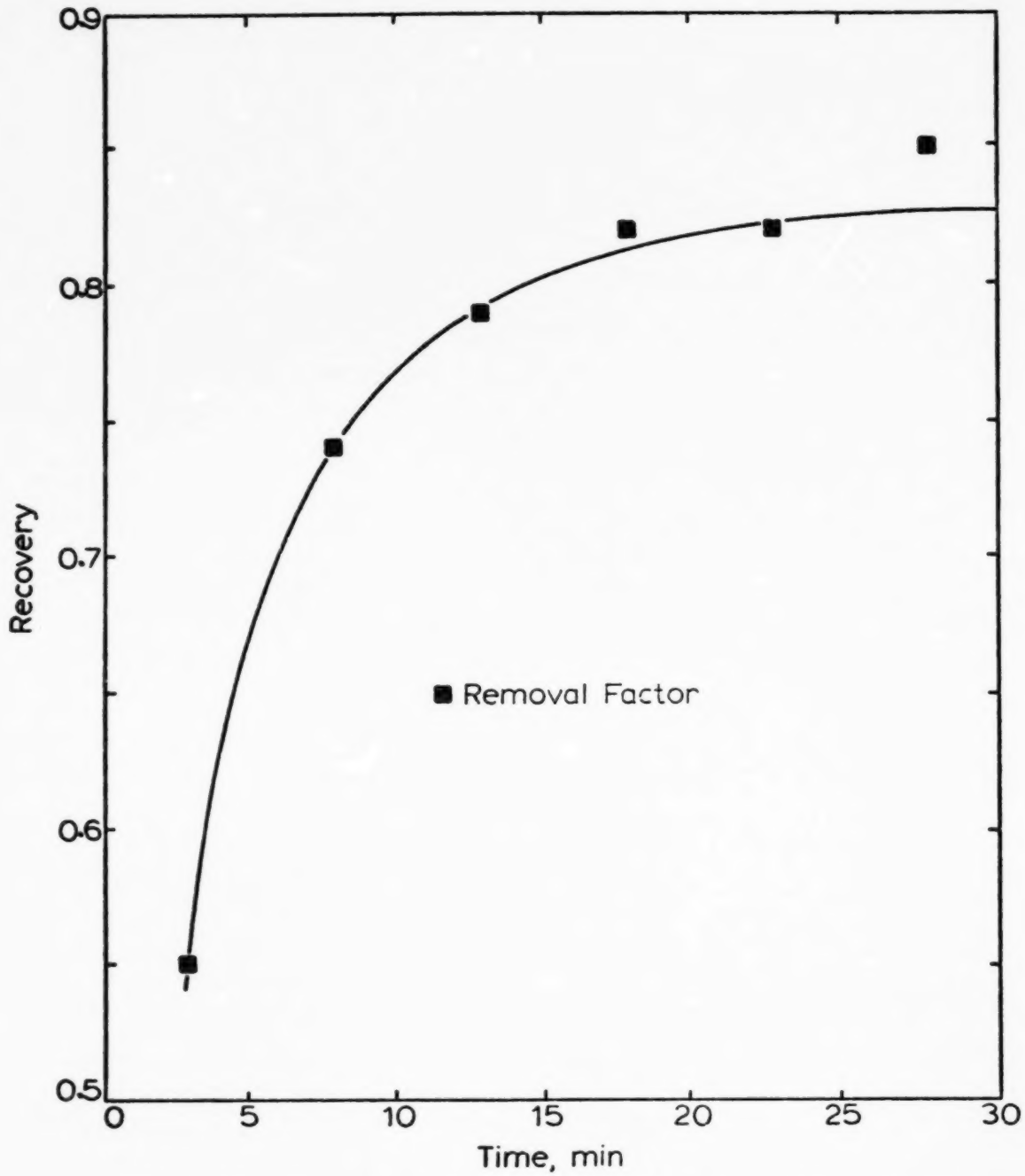

Figure 19. The effect of conditioning time on cyanide recovery.

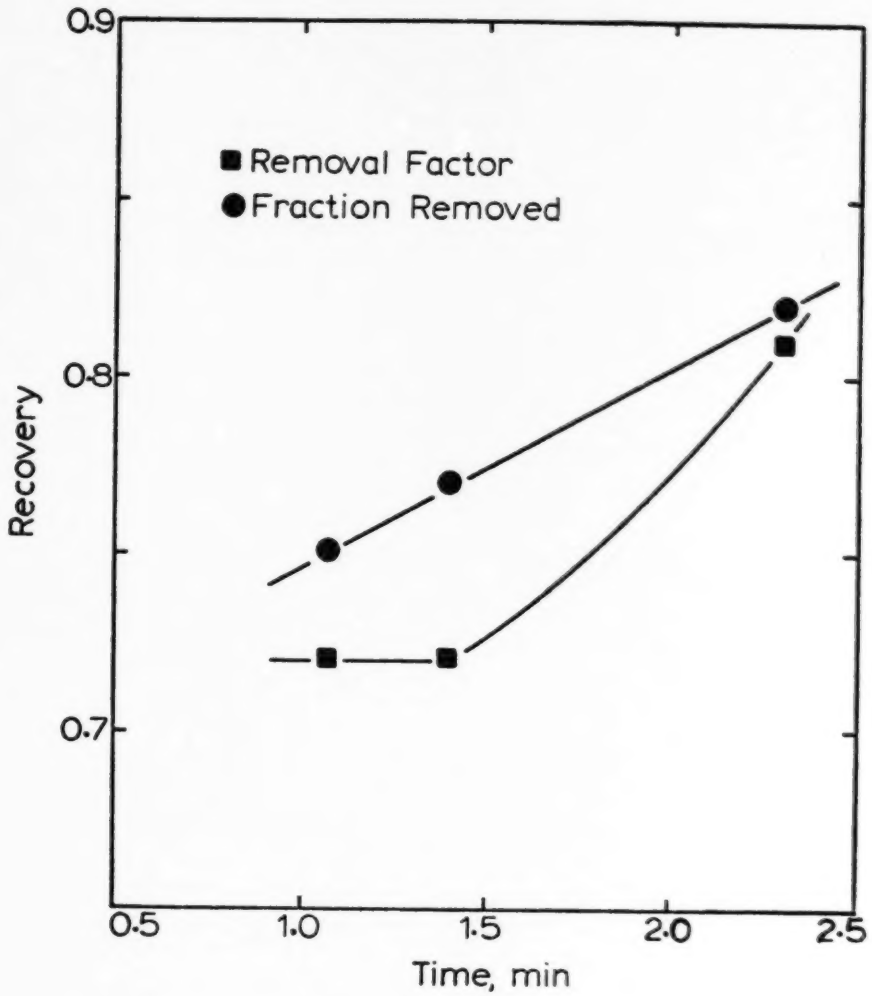

Figure 20. The effect of flotation time on cyanide recovery.

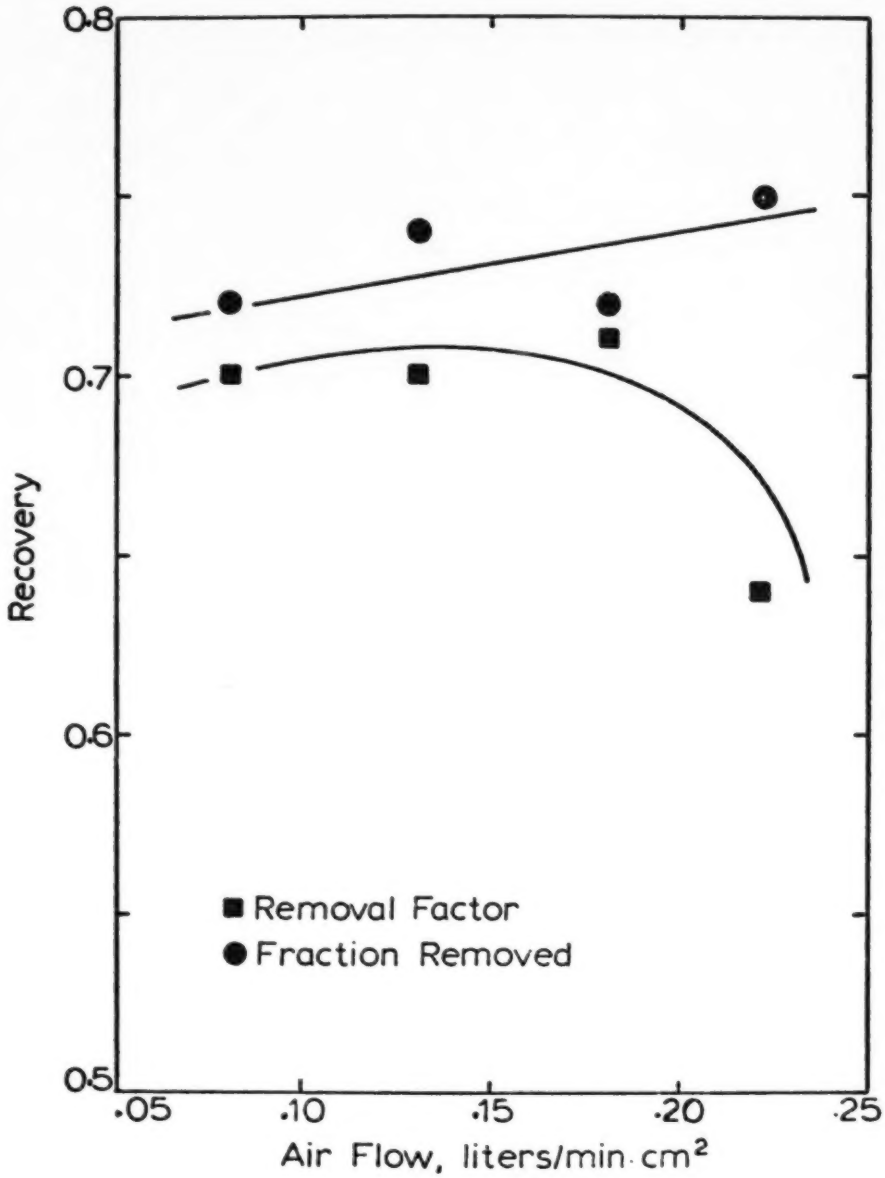

Figure 21. Cyanide recovery as a function of air rate.

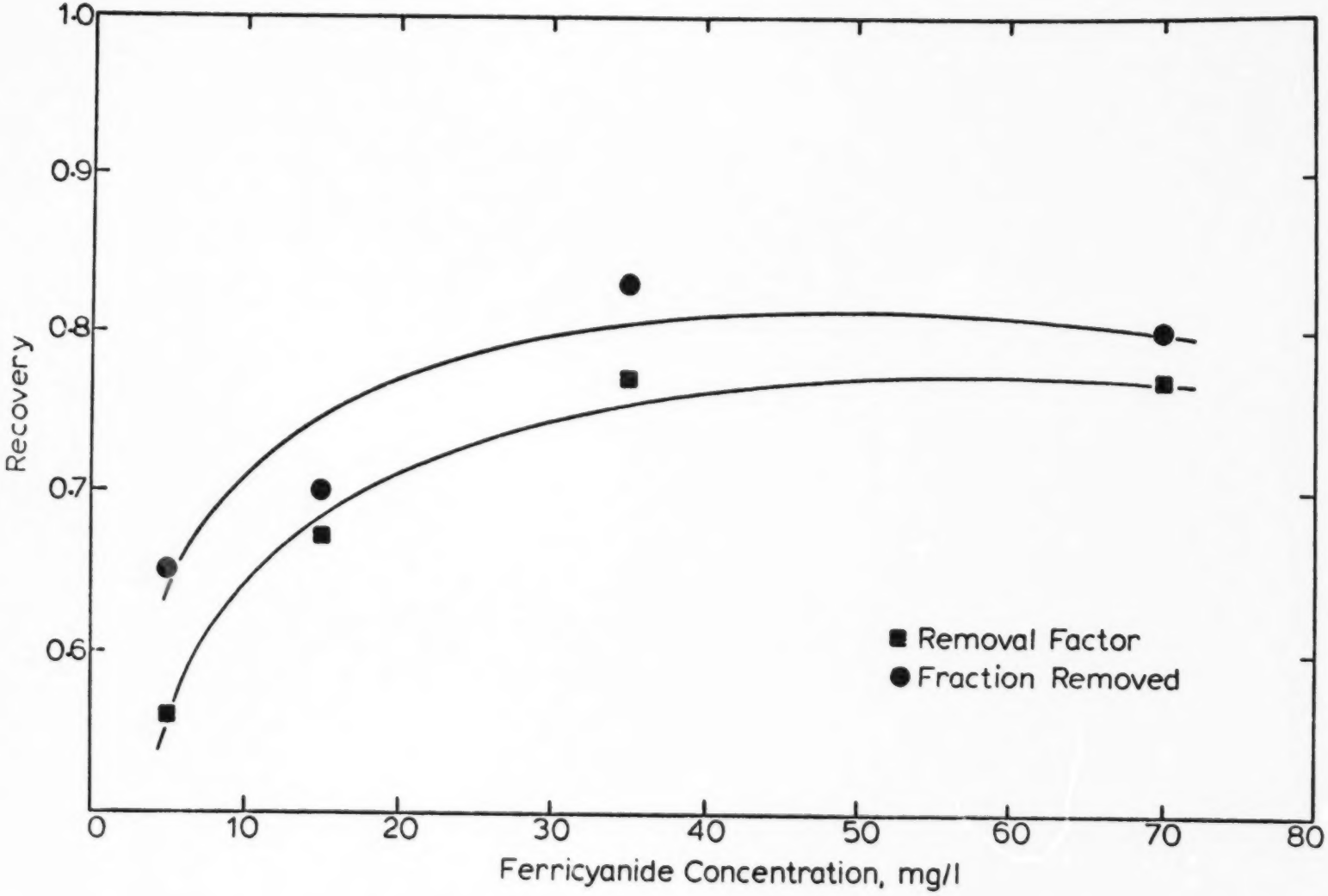

Figure 22. The effect of ferricyanide concentration on cyanide recovery.

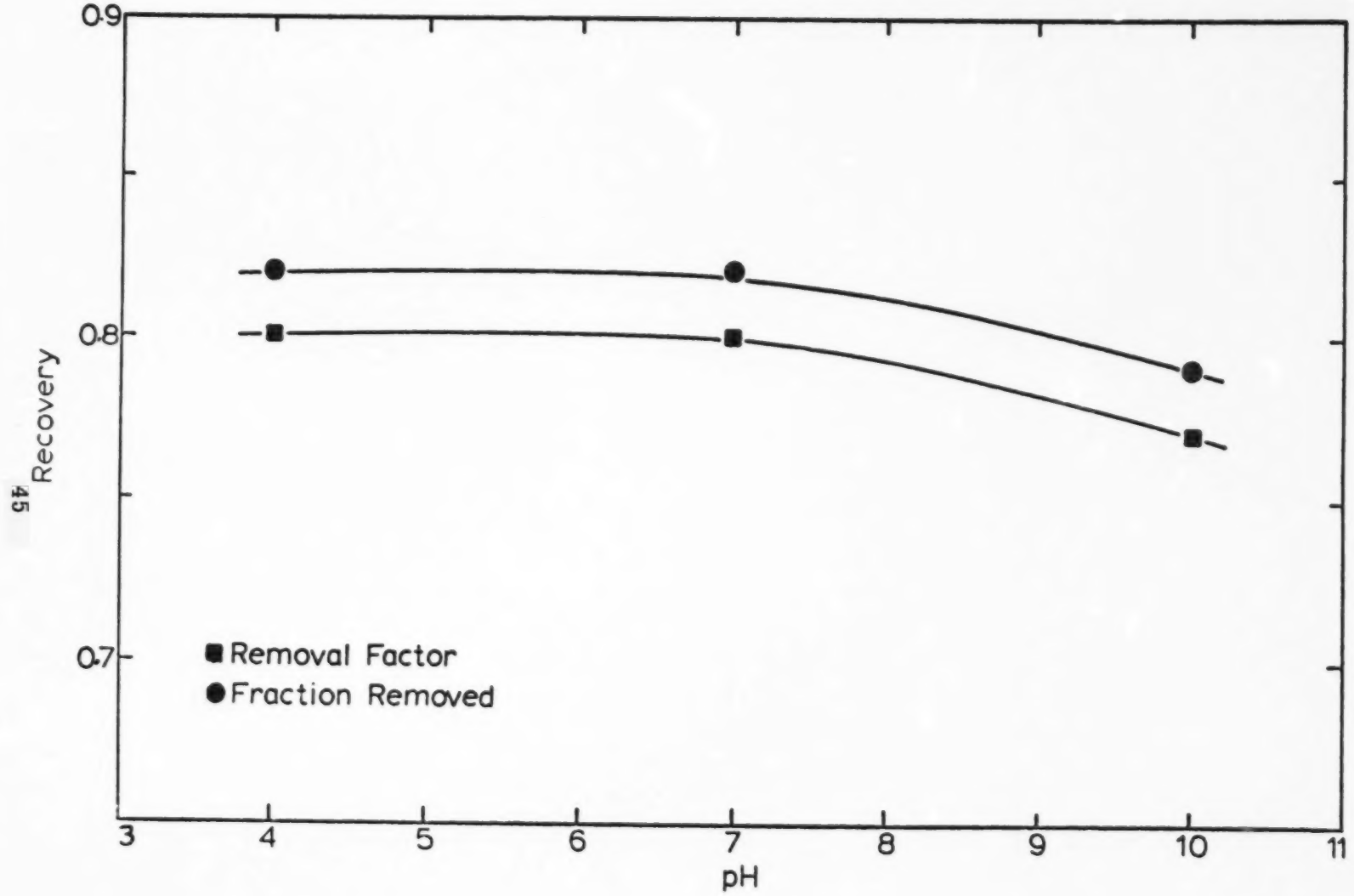

Figure 23. Cyanide recovery as a function of pH.

Ion Flotation of Cyanide and Ferrocyanide

A limited amount of work was done on ion flotation of cyanide ion and ferrocyanide. Cyanide ions did not float well at all, probably because of ion hydration. Ion flotation of ferrocyanide resulted in recoveries comparable to ferricyanide under the same conditions. However, reaction times were much longer. Cyanide can easily be converted to ferrocyanide by addition of ferrous iron whereas conversion to ferricyanide is difficult. Therefore, if some form of ferrocyanide could be efficiently removed by flotation both the free and complexed cyanide could be removed. Consequently the major effort in the project was directed toward microparticulate flotation of iron ferrocyanide precipitates as reported in Section 5.

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APPENDIX A

SYNTHETIC FERROCYANIDE SOLUTIONS

This appendix is a compilation of the data shown in Figures 2, 3, and 4 on cyanide recovery from synthetic ferrocyanide solutions containing 100 mg/ℓ total cyanide.

Effect of pH	(Table A-1)	(Figure 2)
Collector Dosage	(Table A-2)	(Figure 3)
Effect of NaCl	(Table A-3)	(Figure 4)

TABLE A-1. · THE EFFECT OF pH ON CYANIDE RECOVERY FROM FERROCYANIDE SOLUTIONS USING COLLECTOR A336

pH	Fraction Removal	Removal Factor
3	0.94	0.91
4	0.94	0.91
5	0.93	0.89
6	0.89	0.85
7	0.54	0.54
8	0.0	0.0

Fe 144 mg/ℓ; A-336 283 mg/ℓ (Figure 2)

TABLE A-2. THE EFFECT OF COLLECTOR DOSAGE ON CYANIDE RECOVERY FROM FERROCYANIDE SOLUTIONS

mg/ℓ A336	Fraction Removal	Removal Factor
70.0	0.79	0.78
141.0	0.95	0.94
283.0	0.94	0.92
565.0	0.94	0.90

A-336; pH 4, Fe-144 mg/ℓ (Figure 3)

TABLE A-3. THE EFFECT OF COLLECTOR DOSAGE ON CYANIDE RECOVERY FROM FERROCYANIDE SOLUTIONS CONTAINING 5000 mg/ℓ, NaCl

mg/ℓ A336	Fraction Removal	Removal Factor
141.0	0.85	0.83
283.0	0.89	0.87
565.0	0.94	0.93
848.0	0.96	0.95

pH 4, Fe-144 mg/ℓ (Figure 4)

APPENDIX B

SYNTHETIC POTASSIUM CYANIDE SOLUTIONS

This appendix presents the data shown in Figures 5 and 6 for cyanide recovery from KCN-NaCl solutions as a function of pH and collector charge.

Anionic Collector N.L.S. (Table B-1) (Figure 5)
Cationic Collector 12-D (Table B-2) (Figure 6)

TABLE B-1. THE EFFECT OF pH ON CYANIDE RECOVERY FROM KCN-NaCl SOLUTIONS USING COLLECTOR N.L.S.

pH	Fraction Removal	Removal Factor
4.0	0.45	0.28
6.0	0.91	0.89
7.0	0.0	0.0
8.0	0.0	0.0

Fe 215 mg/ℓ, N.L.S. 46 mg/ℓ

TABLE B-2. THE EFFECT OF pH ON CYANIDE RECOVERY FROM KCN-NaCl SOLUTIONS USING COLLECTOR 12-D

pH	Fraction Removal	Removal Factor
4	.87	.85
6	.90	.89
7	.94	.94
8	.99	.99
9	.97	.97
10	.86	.84

Fe 215 mg/ℓ, 12-D 31 mg/ℓ

APPENDIX C

INTERCEPTING SUMP WATER

This appendix presents the data as shown in Figures 7 and 8 on cyanide recovery from intercepting sump water using collector 12-D.

Effect of pH	(Table C-1)	(Figure 7)
Effect of Reaction Time	(Table C-2)	(Figure 8)

TABLE C-1. THE EFFECT OF pH ON CYANIDE RECOVERY FROM INTERCEPTING SUMP WATER

pH*	Fraction Removal	Recovery Factor
5.0	0.67	0.64
5.5	0.58	0.53
6.0	0.82	0.80
6.5	0.86	0.84
7.0	0.91	0.90
7.5	0.69	0.66
8.0	0.67	0.65

*Average of Two Tests Fe 200 mg/ℓ, 12-D 24 mg/ℓ

TABLE C-2. THE EFFECT OF REACTION TIME ON CYANIDE RECOVERY FROM INTERCEPTING SUMP WATER

Minutes*	Fraction Removal	Removal Factor
5.0	.91	.89
15.0	.91	.90
30.0	.92	.91
45.0	.83	.80

*Average of Two Tests pH 7, Fe 200 mg/ℓ, 12-D 24 mg/ℓ